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AMMONIA AND THE NITRIDES

WITH SPECIAL REFERENCE TO
THEIR SYNTHESIS

BY

EDWARD B. MAXTED
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WITH SIXTEEN ILLUSTRATIONS

LONDON
J. & A. CHURCHILL
7 GREAT MARLBOROUGH STREET
1921

PREFACE

THE synthesis of ammonia from its elements possesses considerable general interest as an example of the practical utility of thermodynamic reasoning in directing the course of technical research. For this reason it is hoped that the present small volume, the first sections of which have been prepared primarily with the object of giving, in an easily accessible form, a short account of the experimental work and general principles underlying the commercial synthesis of ammonia, will be acceptable not only to those readers who are directly interested by the problem of nitrogen fixation, but also to students about to enter industrial life.

In view of adequate treatment elsewhere, for instance in Lunge's admirable treatise, no attempt has been made in the present volume to deal with aspects other than the direct synthesis and the conditions which govern the position of the equilibrium point.

The nitrides—which in almost every case may be regarded as ammonia in which hydrogen has been completely replaced by another element—have, on the other hand, been treated from a broader standpoint. The general impression derived from a study of the literature of the subject is the meagreness of our knowledge of these important compounds. In a number of instances little or no work has been published for very many years, and it cannot be doubted that renewed and systematic study of these bodies would amply repay the time and labour expended on such work.

The final chapter on active nitrogen has been included by reason of the interest which is attached to the direct formation of nitrides by interaction of this remarkable modification of nitrogen with various elements.

E. B. M.

Walsall.

CONTENTS

PAGE

PREFACE

CHAPTER I.

THE AMMONIA EQUILIBRIUM 1–20

Calculation of the reaction constant from the temperature coefficient of the heat of formation of ammonia; calculation of the reaction constant from the difference in specific heats of reactants and resultants; experimental determination of the ammonia equilibrium; determinations at higher pressures; derivation of equilibrium percentage of ammonia from value of reaction constant.

CHAPTER II.

THE SYNTHESIS OF AMMONIA UNDER CONDITIONS SUCH THAT EQUILIBRIUM IS NOT ESTABLISHED . . 21–48

Further types of pressure furnaces; Haber and Le Rossignol's circulating system; kinetics of ammonia formation; influence of temperature on the yield; influence of composition of reacting mixture; influence of pressure; efficiency of catalysts; osmium; iron; uranium; cerium; manganese; tungsten; synthesis of ammonia at very high temperatures; synthesis by silent discharge.

CHAPTER III.

THE NITRIDES 49–6

Formation by direct union of the elements; thermal synthesis of nitrides; preparation by interaction of ammonia with the element; formation by the action of ammonia on an oxide or salt; formation by decomposition of amides or imides; general properties of nitrides.

PAGE

CHAPTER IV.

NITRIDES OF GROUPS I, II AND III OF THE PERIODIC SYSTEM 61–76

Nitrides of the alkali metals; copper nitride; silver nitride; nitrides of gold; nitrides of the alkaline earths; beryllium nitride; magnesium nitride; zinc nitride; cadmium nitride; mercury nitride; boron nitride; aluminium nitride; nitrides of the rare earths.

CHAPTER V.

NITRIDES OF GROUPS IV, V AND VI OF THE PERIODIC SYSTEM 77–92

Cyanogen; silicon nitride; nitrides of titanium; nitrides of zirconium; cerium nitride; thorium nitride; tin nitride; lead nitride; nitrides of vanadium; niobium nitride; nitrides of tantalum; phosphorus nitride; arsenic nitride; antimony nitride; bismuth nitride; chromium nitride; molybdenum nitride; tungsten nitride; uranium nitride; sulphides of nitrogen; nitrogen selenide; nitrogen telluride.

CHAPTER VI.

NITRIDES OF GROUPS VII AND VIII OF THE PERIODIC SYSTEM 93–101

Magnesium nitride; nitrides of the halogens; iron nitride; nickel nitride; cobalt nitride

CHAPTER VII.

ACTIVE NITROGEN 102–112

Activation of nitrogen by condensed discharge at low pressures; chemical properties of active nitrogen; combination with mercury, zinc, cadmium, sodium, phosphorus and sulphur; luminous effects; concentration of active modification; activation dependent on the presence of a trace of oxygen or other impurity; preparation of an active modification by electrolysis of an azide.

AMMONIA AND THE NITRIDES

CHAPTER I.

THE AMMONIA EQUILIBRIUM.

THE theoretical calculation of the reaction constant,

$$K_c = \frac{C_{NH_3}}{C_{N_2}^{\frac{1}{2}} \times C_{H_2}^{\frac{3}{2}}},$$

is based on van 't Hoff's isochore,

$$\frac{d \log_e K_c}{d T} = - \frac{Q_{(v)T}}{RT^2},$$

the integration of which depends on a knowledge of the variation with temperature of the heat of formation of ammonia from its elements, a relation which may either be determined directly or calculated by Kirchhoff's equation, from a knowledge of the temperature coefficients of the specific heats of nitrogen, hydrogen and ammonia respectively.

In the above equation, K_c represents the quantity obtained by expressing the nitrogen, hydrogen and ammonia content of an equilibrium mixture by concentrations, for instance, as mols per litre rather than as partial pressures. The slight modification necessary for calculating the more convenient reaction constant K_p, based on partial pressures, is treated below. $Q_{(v)T}$ refers to the heat of formation at constant volume at temperature T.

The heat of formation at constant pressure of 1 grm. molecule of gaseous ammonia at 18° C. is given by Thomsen* as 11,890 calories. Berthelot and Matignon,† who also determined this quantity by the direct combustion of ammonia in oxygen, obtained the somewhat higher figure of 12,200 cals. for the same temperature.

Probably the most accurate determinations of the heat of formation of ammonia at various temperatures are those of Haber, Tamaru and Ocholm,‡ who subjected a current of ammonia to a process of catalytic decomposition in a calorimeter maintained at the temperature in question, the heat absorbed by the decomposition of the ammonia being compensated for by electrically heating the osmium catalyst in such a way that the thermal equilibrium of the system remained undisturbed by the decomposition. The amount of electrical energy thus supplied per second, expressed in heat units, is equal to the heat of formation of the mass of ammonia decomposed

TABLE I.

Temperature.		$Q_{(p)T}$.		
°C.	°Abs.	Observed.	Calculated by equation (a).	Calculated by equation (b).
0	273	10,950	10,950	10,950
466	739	12,670	12,669	12,670
503	776	12,700§	12,773	12,773
554	827	12,900	12,906	12,905
659	932	13,150	13,151	13,152

---

* Thermochemistry, English edition, translated by K. Burke, p. 245.

† Ann. Chim. et Phys. (5), 1880, 20, 253.

‡ Z. f. Elektrochem, 1915, 21, 191, 206.

§ This value does not fall on the general curve.

during the same unit of time, this latter quantity being easily determined with a high degree of accuracy by measuring the volume of hydrogen and nitrogen produced.

Table I summarises the results obtained.

The observed results may be represented by the relation,

$$Q_{(p)t} = 10{,}950 + 4{\cdot}54t - 0{\cdot}001822t^2 \quad . \quad . \quad (a)$$

or, if temperature is measured in degrees absolute,

$$Q_{(p)T} = 9575 + 5{\cdot}535T - 0{\cdot}001822T^2 \quad . \quad (b)$$

Starting from the fundamental relation,

$$R\frac{d\log_e K_c}{dT} = -\frac{Q_{(v)T}}{T^2},$$

we have for the reaction $\frac{3}{2}H_2 + \frac{1}{2}N_2 = NH_3$

$$Q_{(p)T} = Q_{(v)T} + RT \quad . \quad . \quad (1)$$

Hence,

$$R\,d\log_e K_c = \left(\frac{R}{T} - \frac{Q_{(p)T}}{T^2}\right)dT \quad . \quad (2)$$

Substituting the empirical expression obtained above, for the variation of $Q_{(p)T}$ with temperature,

$$R\,d\log_e K_c = RT^{-1}dT - (9575T^{-2} + 5{\cdot}535T^{-1} - 0{\cdot}001822)dT.$$

Integrating, we obtain—

$$R\log_e K_c = R\log_e T + 9575T^{-1} - 5{\cdot}535\log_e T + 0{\cdot}001822T + \text{const.} \quad (3)$$

In order to substitute for K_c the more convenient reaction constant K_p, based on partial pressures, slight additional treatment is necessary.

If p be the partial pressure of a component of a mixture obeying Boyle's law, and c its concentration in mols per litre,

$$c = \frac{p}{RT}$$

Hence, for the formation of one molecule of ammonia,

$$K_c = \frac{\frac{P_{NH_3}}{RT}}{\left(\frac{P_{H_2}}{RT}\right)^{\frac{3}{2}} \times \left(\frac{P_{N_2}}{RT}\right)^{\frac{1}{2}}} = K_p \times RT.$$

Substituting $RT \times K_p$ for K_c in equation (3)

$$R \log_e (RT \cdot K_p) = R \log_e T + 9575T^{-1} - 5{\cdot}535 \log_e T + 0{\cdot}001822T + \text{const.}$$

Cancelling the common term $R \log_e T$ and adding the constant $R \log_e R$ to the integration constant,

$$\log_e K_p = \frac{9575}{RT} - \frac{5{\cdot}535}{R} \log_e T + \frac{0{\cdot}001822T}{R} + \text{const.},$$

or, replacing the natural logarithms by logarithms to base 10,

$$\log_{10} K_p = \frac{2095}{T} - 2{\cdot}7884 \log_{10} T + 0{\cdot}0003986T + \text{const.} \quad . \quad . \quad . \quad (4)$$

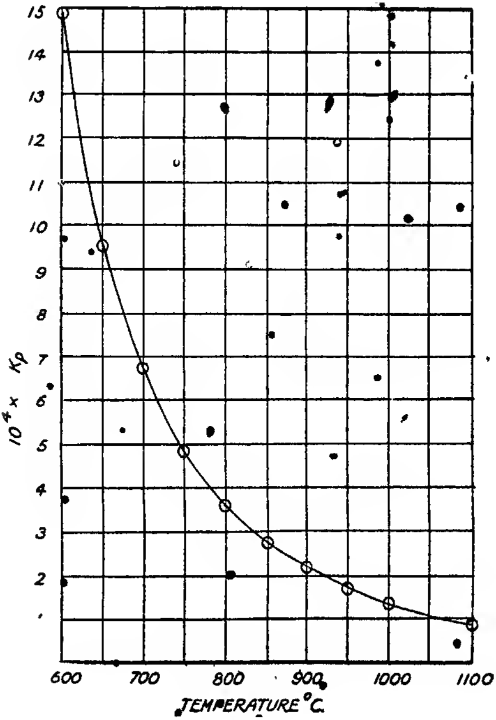
The constant term may be evaluated approximately by means of the Nernst heat theorem, or may be conveniently and accurately inserted from a determination of the ammonia equilibrium at any one temperature. From the measurements of Haber and his collaborators, K_p for 850° C. is approximately 0·000273, from which by substitution the constant term of equation (4) is seen to be 2·6253. We have accordingly, as the final expression for calculating K_p at any required temperature,

$$\log_{10} K_p = \frac{2095}{T} - 2{\cdot}7884 \log_{10} T + 0{\cdot}0003986T + 2{\cdot}6253 \qquad (5)$$

Fig. 1 shows in graphical form the variation of K_p with temperature calculated in this way. The close agreement between the calculated values of K_p and those determined experimentally will be considered later.

As an alternative to the derivation of K_p from direct experimental measurements of the variation of the heat of formation with temperature, the latter

FIG. 1.



quantity may be calculated by Kirchhoff's equation from the variation with temperature of the specific heats of nitrogen, hydrogen and ammonia, provided that the heat of formation of ammonia at any one temperature is known.

From Holborn, Austin and Henning's determinations of the specific heat of nitrogen, the true molecular heat of this gas between 0° and 1400° C., and at constant pressure, may be represented by the relation,

$$C_p = 6·58 + 0·00106t \quad . \quad . \quad . \quad . \qquad (6)$$

The result is somewhat less than Regnault's earlier value of 6·84 for the mean molecular heat between 0° and 200° C., but corresponds well with Pier's figure of 6·02 for the mean molecular heat at constant volume between 0° and 2500° C., the molecular heat at constant volume being connected with that at constant pressure by the equation:

$$C - C_v = R,$$

in which R is the gas-constant, the value of this in heat units being 1·985.

For the true molecular heat of hydrogen at constant pressure, the expression

$$C_p = 6·8 + 0·0006 \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

agrees well with Regnault's value of 6·87 for the mean molecular heat between 12° and 200° C., and with Haber and Tamaru's direct measurement of 7·03 for the true molecular heat at 422° C., but leads to a slightly lower value than corresponds to Wiedemann's figure 6·87 for the mean molecular heat between 21° and 100° C.

The molecular heat of ammonia changes far more rapidly with temperature than that of hydrogen or nitrogen, its value at various temperatures being given in Table II.

Haber and Tamaru's relation,

$$C = 8·62 + 0·0035t + 5·1 \times 10^{-6}t^2 \quad . \qquad (8)$$

is in fairly good agreement with all the above values.

According to Kirchhoff's equation:

$$Q_{(p)t} = Q_{(p)} + \Delta_c t \quad . \quad . \quad . \qquad (9)$$

TABLE II.

Temperature, ° C.	True C_p.	Observer.
0	8·54	Wüllner
100	9·07	"
200	9·59	"
309	10·3	Haber and Tamaru
422	11·0	" "
523	11·8	" "

in which Δ_t represents the difference between the mean molecular heats of factors and products respectively, between 0° and t°.

Accepting relations (6), (7) and (8) for the true molecular heats of nitrogen, hydrogen and ammonia, the mean molecular heats of these gases between 0 and t° C. become:

For nitrogen $6{\cdot}58 + 0{\cdot}00053t$.
For hydrogen $6{\cdot}8 + 0{\cdot}0003t$.
For ammonia $8{\cdot}62 + 0{\cdot}00175t + 1{\cdot}7 \times 10^{-6}t^2$.

Accordingly, for the reaction:

$$\tfrac{3}{2}H_2 + \tfrac{1}{2}N_2 = NH_3$$

$$\Delta_t = 4{\cdot}87 - 0{\cdot}001035t - 1{\cdot}7 \times 10^{-6}t^2 \quad . \qquad (10)$$

Table III gives the values of $Q_{(p)}$ for various temperatures, calculated by introducing equation 10 into Kirchhoff's equation, the resulting expression being—

$$Q_{(p)t} = Q_{(p)0} + 4{\cdot}87t - 0{\cdot}001035t^2 - 1{\cdot}7 \times 10^{-6}t^3 \qquad (11)$$

$Q_{(p)0}$ has been taken as 10,950 calories.

The value of $Q_{(p)}$, thus calculated, is the sum of three terms, *i. e.* the variation of the specific heats of the various gases with temperature, none of which is known with very great accuracy. For this reason the values obtained only agree approximately with those observed experimentally, but the degree of approximation is such as to render possible a sufficiently accurate calculation of K_p on this basis.

TABLE III.

Temperature, ° C.	$Q_{(p)}$.	
	Calc. by eq. (11).	Observed.
	$10^3 \times$	$10^3 \times$
0	10·9	10·9
100	11·4	—
200	11·9	—
466	12·8	12·7
554	13·0	12·9
659	13·2	13·1

It is obvious that equation (11) may be used for integrating the van 't Hoff isochore in the manner dealt with above, very similar values for K_p being obtained by either method.

Haber's equation for the variation of K_p with temperature is—

$$\log_{10} K_p = \frac{2098}{T} - 2{\cdot}5088 \log_{10} T - 0{\cdot}0001006\, T + 0{\cdot}186 \times 10^{-6} T^2 + 2{\cdot}1 \quad . \quad (12)$$

This relation may, for cases where great accuracy is not required, be employed in the abbreviated and approximate form—

$$\log_{10} K_p = \frac{2888}{T} - 6{\cdot}134 \quad . \quad . \quad (13)$$

In view of the variation with pressure of the specific heats of hydrogen, nitrogen and ammonia, the above equations will not be strictly valid for very high pressures, since the gases employed have been supposed to obey the simple gas laws without the introduction of van der Waals' or similar equations. The agreement between the calculated and observed values of K_p at, for instance, 30 atmospheres is, however, strikingly close.

It is, further, to be noted that all the above equations expressing the variation of Q_t with temperature are of such a nature that they pass through a maximum, then decrease, and at a still higher temperature pass through zero and become negative. This point is of considerable interest in connection with the formation of ammonia at very high temperatures, including its existence in the sun, since, by the Le Chatelier-Braun principle, the equilibrium percentage of ammonia should decrease with increasing temperature so long as the reaction is exothermic, but should pass through a maximum value and rise once more with any reversal at high temperatures of the sign of Q_t. This point, which will be discussed in greater detail in connection with the synthesis of ammonia at very high temperatures, such as obtain in arc and other flames, may also be obtained directly from the form of the van 't Hoff isochore.

THE EXPERIMENTAL DETERMINATION OF THE AMMONIA EQUILIBRIUM.

The work in question divides itself from an experimental standpoint into measurements carried out at atmospheric pressure and into those made at pressures greater than atmospheric respectively. In each case the reaction constant,

$$K_p = \frac{P_{NH_3}}{P^{\frac{3}{2}}_{H_2} \times P^{\frac{1}{2}}_{N}},$$

will, with the reservations made above, be the same for a given temperature, but the actual percentage of ammonia obtained will vary with the pressure according to the relation—

$$\text{Percentage } NH_3 = \frac{100\ P_{NH_3}}{P},$$

in which P is the total pressure of the system.

The first determinations of the ammonia equilibrium at atmospheric pressure would appear to be those of Haber and van Oordt,* who measured the limit of decomposition obtainable by passing ammonia over an iron catalyst maintained at a temperature just above 1000° C., this limit being compared with the maximum amount of ammonia formed by slowly passing a mixture of nitrogen and hydrogen over a similar catalyst under similar conditions of temperature. The work was extended by Haber and Le Rossignol.†

The experimental apparatus, which was substantially the same both for Haber and van Oordt's and for Haber and Le Rossignol's work, is shown diagrammatically in Fig. 2.

Ammonia, obtained by decomposing the unstable compound of this body with ammonium nitrate, was led from the generating flask, shown on the extreme right of the diagram, through the upper of the two similar tubes, each of which contained a catalyst plug. The two tubes were heated in an electric furnace to the same constant temperature. The ammonia, on passing through the catalyst plug contained in the upper of the two tubes, was decomposed to an extent depending on the temperature and on the velocity of passage, and on sufficiently reducing the latter it was found that any further decrease in the ammonia rate failed to give a corresponding increase in the decomposition, the equilibrium value being thus reached from the ammonia side. This maximum decomposition, corresponding to a given temperature, was measured by absorbing the ammonia in the exit gas by means of standard acid contained in B. In order to determine the equilibrium from the nitrogen-hydrogen side, the gas resulting from the above decomposition was, after elimination of its ammonia content, allowed to pass through the lower of the two tubes, the ammonia thus synthesised being measured by absorption in standard acid contained in G. It was again found that the percentage of ammonia obtained at a given temperature approached a maximum on decreasing the rate of passage of the gas mixture, this maximum agreeing substantially with the equilibrium value previously found from the decomposition side. Some typical results of Haber and Le Rossignol's measurements are given in Table IV.

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* Z. f. anorg. Chem., 1905, 44, 341; 42, 111.

† Berichte, 1907, 30, 2144.

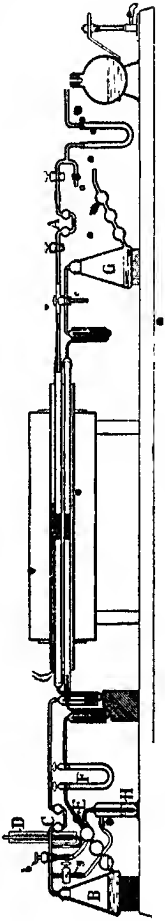


FIG. 2.

Further work on the ammonia equilibrium at atmospheric pressure was carried out by Haber and Maschke.* In this case the mixture of hydrogen and nitrogen, for determinations carried out from

---

* Z. f. Elektrochem., 1915, 21, 128.

TABLE IV.

Temperature, °C.	Catalyst.	$10^4 \times K_p$ (decomposition).	$10^4 \times K_p$ (synthesis).
700	Manganese	7·1	6·6
750	”	4·77	4·77
800	”	3·31	3·58
804	Iron	3·17	3·27
850	”	2·76	2·85
850	”	2·87	2·90
850	Nickel	2·94	2·80
850	Manganese	2·83	2·90
930	Iron	2·02	1·90
930	Nickel	1·80	1·85
1000	Iron	1·42	1·47
1000	Nickel	1·42	1·44
1000	Chromium	1·46	1·39

the synthesis side of the equilibrium side, was prepared by interaction of electrolytic hydrogen and air in proportions sufficient to give a mixture containing about 75 per cent. of hydrogen and 25 per cent. of nitrogen. The gas was freed from the last traces of oxygen by passage over heated palladium-asbestos, followed by concentrated sulphuric acid and soda lime. For determinations of the equilibrium from the ammonia side, a similar mixture was employed to which 0·28 per cent. of ammonia had been added, the mixture being contained for convenience in a compressed condition in a steel cylinder. In this case the drying was effected by means of barium oxide. The determinations were carried out in a glazed porcelain tube about 10 mm. in internal diameter, which was heated in an electric furnace in such a way that a zone of temperature, constant to within 1° and about 6 cm. long, was maintained within the tube. The catalysts employed were iron-asbestos or uranium carbide, which were kept in position by means of plugs of pure asbestos. The temperature was measured by means of a thermo-couple placed on the external wall of the porcelain tube, the whole being mounted in an iron mantle in order to ensure constancy of temperature.

Haber and Maschke's results are given in Table V. The fifth column of this table contains values for the equilibrium constant calculated by means of the expression—

$$\log_{10} K_p = \frac{2095}{T} - 2{\cdot}7884 \log_{10} T + 0{\cdot}0003986\,T + 2{\cdot}6253 \qquad (5)$$

developed earlier in the present chapter, while the fourth column contains similar values calculated by Haber's equation:

$$\log_{10} K_p = \frac{2098}{T} - 2{\cdot}5088 \log_{10} T - 0{\cdot}0001006\,T + 0{\cdot}186 \times 10^{-6}T^2 + 2{\cdot}1 \qquad (12)$$

For the purpose of comparison, the values for the equilibrium constant obtained from smoothed curves based on Haber and Le Rossignol's earlier results have also been included (Table V).

In order to facilitate conversion of the equilibrium constant into percentage of ammonia, Table VI is given for a system having a total pressure of 1 atmosphere, the composition consisting originally of hydrogen and nitrogen in the stoichiometric proportions of 3 to 1.

Reference may also be made to Table VIII, in which is given the calculated equilibrium percentage of ammonia corresponding to various temperatures and pressures.

The equilibrium determinations at 30 atmospheres pressure are probably, by reason of their precision

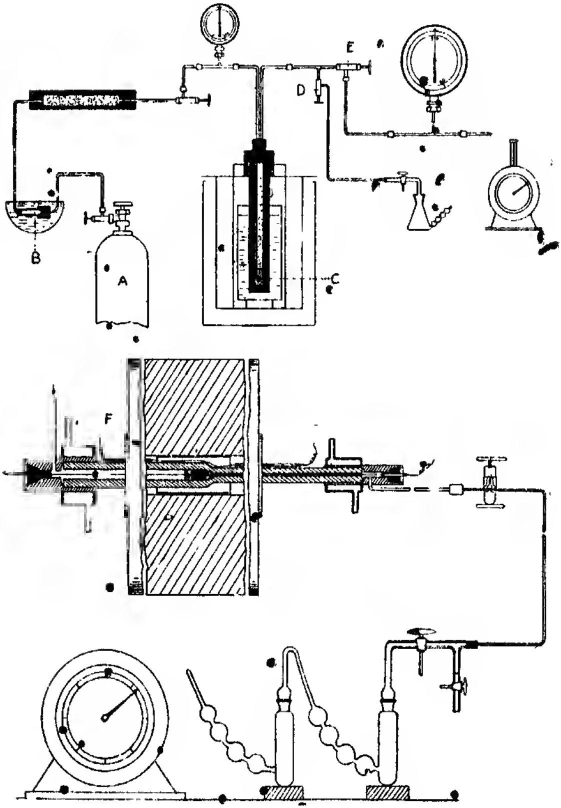
TABLE V.

Temperature, °C.	$K_p \times 10^4$.			
	Observed by Haber and Le Rossignol.	Observed by Haber and Maschke.	Calc. by equation (12).	Calc. by equation (5).
600	—	13·6	15·2	14·9
700	6·8	6·57	6·84	6·83
750	4·68	—	4·98	4·88
800	3·34	—	3·62	3·59
850	2·79	2·71	2·73	2·71
930	2·00	—	1·84	1·81
1000	1·48	1·39	1·40	1·32
1100	—	0·93	0·93	0·89

TABLE VI.

$10^4 \times K_p$.	Corresponding percentage of ammonia.
200	0·7
100	0·32
50	0·14
40	0·11
30	0·08
20	0·06
10	0·032
9	0·029
8	0·025
7	0·023
6	0·019
5	0·016
4	0·013
3	0·0096
2	0·0065
1	0·0036

FIG. 3.



and of the care with which they were made, even more accurate than those which have just been considered. Haber's earlier work at this pressure was carried out in collaboration with Le Rossignol, and the results obtained were confirmed by later measurements in conjunction with Tamaru and Ponnaz.* The apparatus employed in the latter determinations is shown diagrammatically in Fig. 3.

It consists of a steel cylinder A, containing, at a pressure of 100 atmospheres or over, a nitrogen-hydrogen mixture, which was made as before by the combustion of electrolytic hydrogen and air in proportions sufficient to give a product containing approximately 75 per cent. by volume of hydrogen and 25 per cent. of nitrogen. This gas was led without reduction of pressure through a heated palladium-asbestos tube B, followed by a soda-lime drier, and subsequently through a small steel furnace C containing osmium. The furnace could, for determinations of equilibrium for the ammonia side, be heated by means of an external bath, and under these conditions, gave a gas containing ammonia in excess of the equilibrium percentage for 30 atmospheres. A valve D enabled this percentage to be determined by absorption of a sample in standard acid. The high-pressure system was at this point reduced by means of a reducing valve E to the standard pressure of 30 atmospheres employed for the measurements, and was next passed into the furnace F used for determining the equilibrium percentage. It will be seen that the gas which reaches this main furnace will be either pure nitrogen-hydrogen mixture, or a mixture containing ammonia in excess of the equilibrium value, according to whether the preliminary osmium tube is cold or is heated to a temperature sufficient to cause synthesis.

The main furnace shown in the diagram consisted of a silica tube heated by means of an external winding of resistance wire. This, for the portion of the tube containing the catalyst, was wound on a mantle of copper foil and covered with the same material, insulation being effected by a layer of asbestos paper. A zone of constant temperature was thus obtained such that a length of 3 cm. did not vary more than about ½° from the mean value. This temperature was measured by means of an external thermo-couple placed with its junction on the outside of the silica tube, at a point corresponding with the position of the catalyst, and by an internal pyrometer wire, stretched through the entire silica tube, as shown, with its junction at the exit side of the catalyst and its ends at opposite ends of the silica tube, into which it was fastened by means of sealing-wax. The ammonia content of the gas issuing from this furnace was estimated in the usual way by absorption in standard acid, the total volume passed being measured by passage through a meter.

---

* Z. f. Elektrochem., 1915, 21. 89.

A second type of furnace of the internally heated type, which did not, however, prove quite so satisfactory from the point of view of constancy of the temperature of the catalyst plug, is shown in Fig. 4. It consists of a thin-walled iron tube, closed at its lower end, and wound with resistance wire with interposition of a copper temperature-equaliser. The gas mixture passes into the entrance tube as marked, and from this, after passing downwards through the iron mantle, doubles upwards into the internal quartz tube and through the catalyst, finally passing out of the system by the lateral exit tube shown at the top of the diagram. The whole is mounted in a pressure-resisting steel shell and is insulated from this by means of a refractory lining. The steel shell is filled with gas at a pressure equal to that obtaining within the reaction space by means of a by-pass provided with the usual ammonia absorption tube, as shown. A feature of this furnace was the possibility of sliding a thermo-couple into any desired position along the internal pyrometer tube.

Temperature and pressure were determined with the greatest care, and the series represents probably the most accurate measurements of the equilibrium constant which have been made.

FIG. 4.

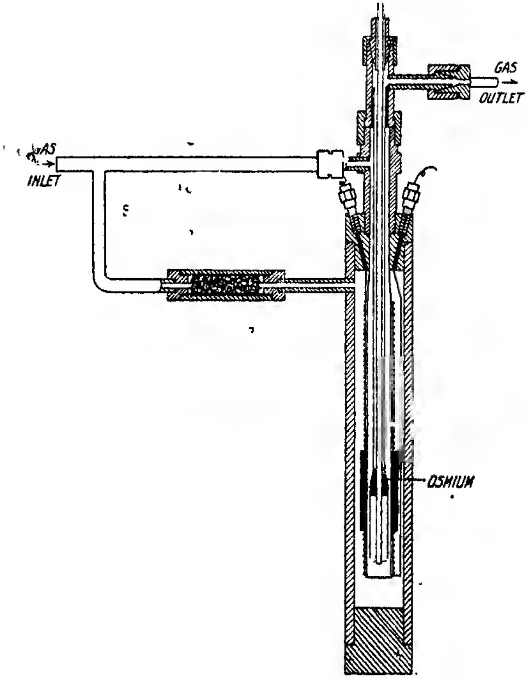


Table VII summarises the results obtained. In this table, for the purpose of comparison, results obtained previously by Haber and Le Rossignol have been included. Osmium was used as the catalyst for all the measurements.

TABLE VII.

Temperature, °C.	$K_p \times 10^4$.				
	Observed.	Calc. by equation (12).	Calc. by equation (5).	Observer.	No. of observations.
561	21·3	21·5	21·1	H. T. & P.	5
620	12·6	12·7	12·6	,,	2
631	11·4	11·65	11·5	,,	3
700	6·8	6·88	6·83	H. & Le R.	6
704	6·56	6·71	6·64	H. T. & P.	3
710	6·46	6·43	6·35	,,	1
722	5·82	5·92	5·87	,,	1
801	3·56	3·60	3·57	H. & Le R.	6
812	3·38	3·38	3·35	H. T. & P.	3
901	2·13	2·11	2·08	H. & Le R.	9
914	1·99	1·99	1·95	H. T. & P.	3
952	1·68	1·66	1·63	,,	3
974	1·48	1·51	1·48	H. & Le R.	6

H. T. & P. = Haber, Tamaru and Ponnaz.
H. & Le R. = Haber and Le Rossignol.

Finally, by insertion of the appropriate value K_p in the equation,

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{\frac{1}{2}} \times p_{H_2}^{\frac{3}{2}}},$$

the percentage of ammonia in equilibrium with nitrogen and hydrogen at a given temperature and pressure may be obtained. Table VIII refers to equilibrium in a system containing hydrogen and nitrogen in the proportion of 3 to 1.

TABLE VIII

Temperature, ° C.	Equilibrium percentage of ammonia.			
	At 1 atm.	30 atm.	100 atm.	200 atm.
200	15·3	67·6	80·6	85·8
300	2·18	31·8	52·1	62·8
400	0·44	10·7	25·1	36·3
500	0·129	3·62	10·4	17·6
600	0·049	1·43	4·47	8·25
700	0·0223	0·66	2·14	4·11
800	0·0117	0·35	1·15	2·24
900	0·0069	0·21	0·68	1·34
1000	0·0044	0·13	0·44	0·87

CHAPTER II.

THE SYNTHESIS OF AMMONIA UNDER CONDITIONS SUCH THAT EQUILIBRIUM IS NOT ESTABLISHED.

IN addition to special apparatus for measurements of equilibrium, Haber and Le Rossignol* also employed various types of electrically-heated testing furnaces, in which the external pressure-resisting wall was kept cool by water circulation or other means, the furnace proper being separated from this pressure-resisting shell by means of insulating material.

A reaction vessel of this type is shown diagrammatically in Fig. 5, from which it will be seen that the compressed gas mixture, entering the tube by way of A, is raised to reaction temperature by means of the resistance-winding B, which consisted of nickel wire, 0·4 mm. in thickness, wound on the thin-walled iron tube C, and insulated from this by means of a wrapping of asbestos paper. The heated gas mixture, after passing through the catalyst D, leaves the system by means of the capillary E. The external shell is shown at F. The space between this and the heated portion of the furnace is occupied by asbestos, and the pressure in this space is maintained at that existing in the catalyst chamber by means of an auxiliary connection G.

A larger furnace, which was used with considerable success for some of the early circulation experiments,

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* Z. f. Elektrochem., 1913, 19, 53.

Fig. 5.

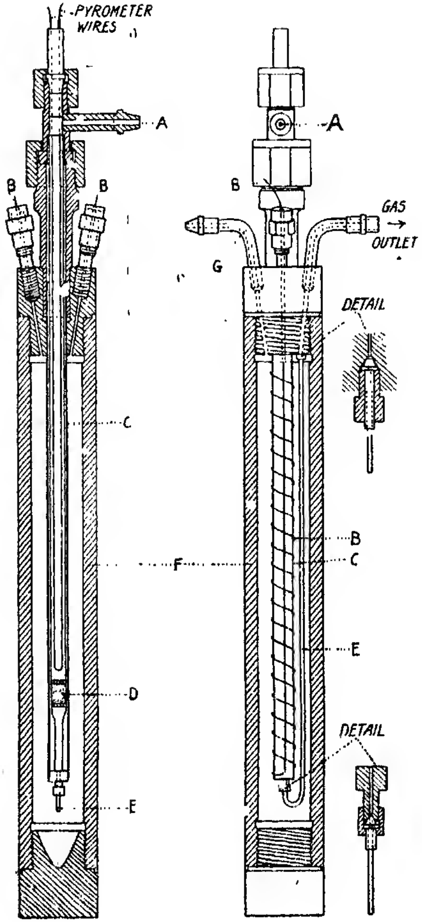
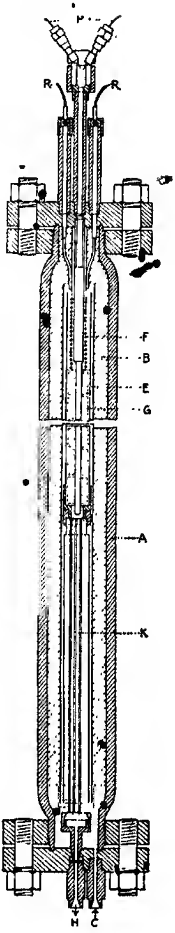

PYROMETER WIRES
A
B
B
C
F
D
E
A
B
GAS → OUTLET
G
DETAIL
B
C
E
DETAIL

FIG. 6.



is illustrated in Fig. 6, and, by reason of its importance, may be described in detail. It differs from the testing tubes dealt with above principally by reason of the inclusion of an internal heat exchanger, by means of which a considerable economy in heating current was effected. The external bomb A measured about 75 cm. long and 6·5 cm. in internal diameter. It was provided with an insulating lining of compressed magnesia-asbestos B, bounded internally by a thin iron tube as shown, the latter containing the furnace proper. The reacting gases passed by way of the gas inlet C, over the outside surface of the heat exchanger K, which consisted of 127 steel capillaries, each of about 1·5 mm. external and 1·1 mm. internal diameter, upwards round the outside E of the catalyst space, then downwards over the heating coil F, through the catalyst space G, and finally through the interior of the steel capillaries to the gas outlet H. A novel feature of the apparatus consisted* in the employment of a series of thermo-couples, by means of which the temperature in the three portions of the furnace, corresponding to the region inside the heating coil itself and to the beginning and end of the catalyst could be measured. The pyrometer and heating connections are shown at P and R respectively.

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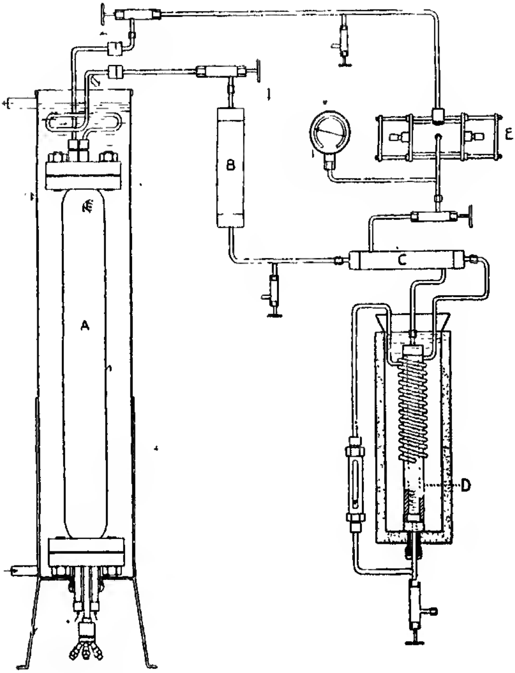
* Haber & Le Rossignol, Z. f. Elektrochem., 1913, 19, 61.

The circulating system, of which the furnace just

Fig. 7.



described formed a part is shown diagrammatically in Fig. 7. The gas is circulated through the system by means of the pump E in such a way as to pass from the synthesising furnace A, which is water-cooled during use, through the circuit-drier B to the "cold" exchanger C and thence to the separator D, which could be cooled to a low temperature by means of an ether-carbon-dioxide mixture. After leaving this refrigerator, once more by way of the exchanger C, the gas re-passed to the circulating pump E and thence again to the furnace. The circulator consisted of a double-acting steel pump having a stroke of 3·6 cm. and a cylinder diameter of 1·9 cm., the piston rod being of steel wire 1·5 mm. in diameter, and passing through stuffing-boxes filled with alternate discs of brass and of cotton soaked in paraffin. According to the dimensions given, each stroke of the pump should circulate about 10 c.c. of compressed gas, but in practice the actual volume circulated was found to be considerably less than this. The ammonia which separated by liquefaction in D could be measured by noting the height of liquid in the gauge attached, fresh gas being continuously added to the system to compensate for that converted into ammonia.

In an experiment with the above apparatus, employing osmium as catalyst, the furnace, which was wound with iron wire 1·1 mm. in thickness, was heated by a current of about 18 ampères from a 56-volt circuit, the temperature registered by the three thermo-junctions being 930°, 780° and 610° C. respectively. On allowing the gases to circulate for a short time without refrigeration, the ammonia percentage rose to 5·4, with a pressure of 185 atmospheres. The refrigerating bath was now filled with a mixture of alcohol and carbon dioxide and maintained at $-30°$ C. Liquid ammonia was found to be produced at the rate of 2–2½ c.c. per minute, with a total of about 500 c.c. for the four hours during which the experiment was continued. The pressure varied from 163 to 193 atmospheres, the circulating pump being operated at the rate of two revolutions per second.

Considered from a kinetic standpoint, the velocity of formation of ammonia decreases somewhat more rapidly with approach towards the equilibrium point than corresponds to the monomolecular equation,

$$\frac{d\,\mathrm{NH}_3}{dt} = \mathrm{K}\ (a-x),$$

in which a represents the concentration of ammonia corresponding to equilibrium. The two curves produced in Fig. 8 illustrate the type of curve obtained with uranium carbide* and with an iron-potash† catalyst respectively, but a more extended investigarion of the progress of ammonia formation with time of contact appears necessary in order to establish the definite kinetic law according to which this takes place. The temperature and pressure for this uranium carbide curve were 114 atmospheres and 515° C., the gas mixture containing 69 per cent. of hydrogen and 31 per cent. of nitrogen, while for the iron-potash result these figures were 180 atmospheres and 550° C., the mixture containing 75 per cent. of hydrogen and 25 per cent. of nitrogen, so that the two curves are not directly comparable with one

TABLE IX.

Time of contact of gas with catalyst in seconds.	Percentage of ammonia formed.	Yield of ammonia in grams per hour per c.c. of catalyst space.
0·34	0·65	2·7
0·56	0·94	2·3
1·8	1·8	1·4
3·6	3·2	1·25
7·2	4·7	0·91
10·8	5·1	0·65
24·5	6·8	0·38

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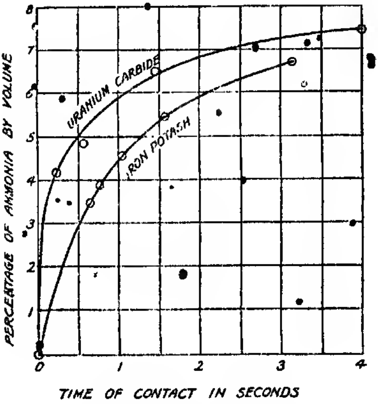
[*] Haber & Greenwood, Z. f. Elektrochem., 1915, **21**, 241.

[†] Maxted, J. Soc. Chem. Ind., 1918, **37**, 232.

another as a measure of the relative activity of the two catalysts.

On calculating the yield of ammonia per unit of time, corresponding to various rates of flow through the catalyst space, it will readily be seen that a long time of contact and consequently a high percentage of ammonia militates against a high yield of ammonia per hour. This is illustrated by Table IX, which is based on the curve given in Fig. 8 for iron-potash.

Fig. 8.



In the following treatment, in accordance with convention, the abbreviations S.V. (space-velocity) and S.T.Y. (space-time-yield) will be employed for expressing the rate of flow of the gases, calculated as litres per hour at room temperature and atmospheric pressure per litre of catalyst space, and for the yield of ammonia expressed in grams per hour per c.c. of catalyst space, respectively.

An increase in the reaction temperature will exert a dual influence on the formation of ammonia, in that while such an increase will react unfavourably on the position of the equilibrium point, reaction velocity itself, for ammonia formation under conditions sufficiently removed from the equilibrium condition, will, on the other hand, become increased thereby. For conditions such as those employed for the technical synthesis, in which the percentage of ammonia formed cannot economically be allowed to approach the equilibrium value for the temperature and pressure employed, by reason of the rapid fall in the value of $\frac{d\,NH_3}{dt}$ as equilibrium is approached, reaction velocity will play as equally important a *rôle* as the position of the equilibrium point in determining the amount of ammonia formed, and an optimum temperature will exist for each catalyst, at which the resultant of these two opposing influences is most favourable to production. As an example of the advantageous effect on the space-time-yield obtained by increasing the reaction temperature for an iron-potash catalyst from 530° to 580° C. the following table is given :*

TABLE X.—*Catalyst : Iron-potash.*

Pressure = 150 atm.

Time of contact in seconds.	T. = 530° C.		T. = 580° C.	
	Per cent. NH_3.	S.T.Y.	Per cent. NH_3.	S.T.Y.
0·6	0·96	2·4	1·5	3·5
1·0	1·3	2·9	2·4	3·3
1·5	1·7	1·7	3·2	2·9
2·0	2·05	1·4	3·8	2·6

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* Maxted, *loc. cit.*

The disadvantageous effect of low temperatures on the space-time-yield and on the ammonia percentage, in spite of the favourable position of the equilibrium point, is also exemplified by the following experiments of Haber and Greenwood* with uranium carbide, these being carried out at exceptionally low temperatures and with comparatively low rates of flow.

TABLE XI.

Temperature ° C.	Pressure, atm.	S.V., $10^3 \times$.	Per cent. NH_3 observed.	S.T.Y
365	140	4	3·0	0·09
415	140	4	9·0	0·26
465	140	4	12·5	0·36

A factor somewhat similar in action to that of increasing the temperature is to be found in increasing the relative proportion of the nitrogen in the nitrogen-hydrogen mixture employed for the synthesis. It can easily be shown theoretically that the optimum gas mixture, from the point of view of the highest possible equilibrium percentage of ammonia corresponding to a given temperature, is that which contains hydrogen and nitrogen in the stoichiometric proportions necessary for ammonia, that is to say 75 per cent. by volume of hydrogen and 25 per cent. of nitrogen, but on the other hand it is found that the velocity of formation of ammonia, especially at stages sufficiently far removed from the equilibrium point, is influenced to a greater degree by the partial pressure of the nitrogen present than by that of the hydrogen. In view of this phenomenon, the percentage of ammonia decreases less rapidly with increasing rate of gas flow for a mixture containing a relatively high proportion of nitrogen than for the 1 : 3 mixture usually employed, this effect being accompanied by a correspondingly greater rate of increase of the space-time-yield. In general, however, this factor is not sufficient, as is often the case with an increased temperature, to compensate for the disadvantageous effect of such an increase in the nitrogen content on the equilibrium percentage of ammonia.

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* Z. f. Elektrochem., 1915, 21, 244.

The point is illustrated by the following comparative figures of Haber and Greenwood :

TABLE XII.—*Catalyst : Uranium Carbide.*

Series I. (Gas mixture = 69·3 per cent. hydrogen, 30·7 per cent. nitrogen.)

Temperature, ° C.	Pressure, atm.	S.V., 10^3 ×.	Time of contact in seconds.	Per cent. NH_3.	S.T.Y.
515	49·6	7·6	86·0	3·93	0·21
515	49·6	24·7	26·4	3·38	0·6
515	49·6	64·8	10·1	2·77	1·28
515	49·6	150·6	4·3	2·0	2·12

Series II. (Gas mixture = 26·5 per cent. hydrogen, 73·5 per cent. nitrogen.)

Temperature, ° C.	Pressure, atm.	S.V., 10^3 ×.	Time of contact in seconds.	Per cent. NH_3.	S.T.Y.
515	49·6	18·0	36·2	1·46	0·19
515	49·6	74·4	8·8	1·36	0·72
515	49·6	147·0	4·4	1·18	1·23

An increase in the working pressure will, unlike a rise of temperature, influence both reaction velocity and equilibrium percentage in the same sense. In view of the apparent complexity of the kinetics of ammonia formation, it is not possible to formulate a relation in which a velocity constant is expressed as a simple function of the pressure, but the general influence of such an increase may be illustrated by the results tabulated in Tables XIII and XIV, which refer to three typical curves for the progress of ammonia formation in presence of uranium carbide at 515° C.,* and to three somewhat similar results with a large grained iron-potash catalyst at 550° C.† The gas mixture in the former case consisted of 69 per cent. of hydrogen and 31 per cent. of nitrogen, while for the latter a 3 : 1 mixture was used.

TABLE XIII.—*Catalyst: Uranium Carbide.*

Pressure, atm.	S.V., $10^3 \times$.	Per cent. NH_3.	S.T.Y.
20·4	4·2	1·82	0·053
20·4	21·6	1·66	0·255
20·4	59·8	1·33	0·55
20·4	126·0	1·06	0·94
49·6	7·6	3·93	0·21
49·6	24·75	3·38	0·6
49·6	64·8	2·77	1·28
49·6	150·6	2·0	2·12
113·6	5·2	7·63	0·28
113·6	28·5	6·42	1·3
113·6	74·4	4·78	2·5
113·6	174·9	4·18	5·2

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* Haber and Greenwood, Z. f. Elektrochem., 1915, 21, 241.

† Maxted, J. Soc. Chem. Ind., 1918, 37, 332.

TABLE XIV.—*Catalyst: Iron Potash.*

S.V. of gas, $10^3 \times$	50 atm.		150 atm.		180 atm.	
	Per cent. NH_3 formed.	S.T.Y.	Per cent. NH_3 formed.	S.T.Y.	Per cent. NH_3 formed.	S.T.Y.
20	2·2	0·34	4·85	0·75	6·7	1·9
40	1·2	0·37	3·7	1·1	5·4	1·65
60	0·8	0·37	2·9	1·35	4·5	2·1
80	0·65	0·4	2·25	1·4	3·9	2·4
100	0·55	0·42	1·8	1·4	3·5	2·7

Efficiency of Catalysts.

The relative activity of various catalysts depends to a very great degree not only on the purity of the material employed and on its method of preparation, but also, of course, by virtue of the relative surface exposed, on the size of granules taken. In the greater number of results published in the literature of the subject this latter factor is not stated, so that the various records of ammonia percentage and of yields obtained in the presence of a given catalyst apply only to this catalyst in an equivalent physical condition and state of subdivision.

Published results relating to the activity of uranium carbide and iron-potash have already been given. In addition to these, the following data may be tabulated as representative of the activity of various catalysts dealt with in published investigations up to the present.

Osmium.

This historically important catalyst was examined by Haber and Le Rossignol.* The metal was employed in fine grains as a plug measuring about 10 mm. in length and 4 mm. in diameter. The measurements were carried out over a period of two and a-half days, during which time the activity was found to increase slightly. The following results are representative of those obtained :

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* Z. f. Elektrochem., 1913, 19, 69.

TABLE XV.—*Catalyst : Osmium.*

Temperature, ° C.	Pressure, atm.	S.V. of gas, 10³ ×	Per cent. NH_3 formed.	S.T.Y.
585	166	24	7·0	1·46
585	166	80	6·2	3·6
585	166	160	4·2	4·8
610	122	160	3·5	4·0
610	156	160	4·05	4·7
610	173	160	4·65	5·3
610	123	240	2·77	4·8

With a catalyst plug 14 mm. long and 4·5 mm. in diameter the yields given in Table XVI were obtained:

TABLE XVI.—*Catalyst : Osmium.*

Temperature, ° C.	Pressure, atm.	S.V. of gas, 10³ ×	Per cent. NH_3 formed.	S.T.Y.
521	174	6·7	9·0	0·43
550	174	6·7	7·9	0·38
572	156	45·0	5·9	1·9
592	156	90·0	4·75	3·1

Iron.

The activity of iron may be influenced greatly by the introduction of various promoters, for details of which the numerous patent specifications of the Badische Anilin- and Soda-Fabrik should be consulted.

As an example of the activity of a promoted iron catalyst, the following figures, obtained by the author, may be cited. The catalyst was employed in granules possessing an average diameter of one-tenth of an inch.

TABLE XVII.

Temperature, ° C.	Pressure, atm.	S.V. of gas, $10^3 \times$	Per cent. NH_3 formed.	S.T.Y.
505	150	10	11·1	0·8
530	150	50	6·9	2·5
530	150	100	5·6	4·3
530	150	200	4·3	6·2
530	150	300	3·8	8·2
530	150	400	3·2	9·2
530	150	500	3·0	10·8
530	150	600	2·7	11·6

Uranium.

In addition to the measurements carried out with uranium carbide, recorded above, Haber and Le Rossignol * investigated the activity of commercial metallic uranium, which was broken into small pieces and used as a plug measuring 3·5 cm. long and 0·45 cm. in diameter. The results, tabulated as before, are given in Table XVIII:

* Z. f. Elektrochem., 1913, 19, 68.

TABLE XVIII.

Temperature, °C.	Pressure, atm.	S.V. of gas, $10_3 \times$	Per cent. NH_3 formed.	S.T.Y.
550	120	3·6	5·85	0·15
550	120	5·4	5·6	0·22
580	120	5·4	4·8	0·19
580	120	36·0	3·5	0·91
580	190	5·4	7·0	0·27
600	190	36·0	5·8	1·5

Cerium.

The following results, together with those of the succeeding sections, dealing with manganese and tungsten, are all taken from Haber and Le Rossignol's paper quoted for uranium. In the case of cerium, the catalyst was prepared by reducing cerium dioxide with magnesium in a current of hydrogen. It was employed as a plug measuring 3·5 cm. in length and 0·5 cm. in diameter. The pressure was in every case 49·5 atmospheres.

TABLE XIX.—*Catalyst: Cerium.*

Temperature, °C.	S.V., $10^3 \times$	Per cent. NH_3.	S.T.Y.
703	14·5	0·53	0·09
703	29·0	0·70	0·15
703	145·0	0·31	0·32
703	220·0	0·19	0·30
800	14·5	0·58	0·06
800	29·0	0·58	0·12
800	145·0	0·45	0·47
800	220·0	0·38	0·60

The yields of ammonia are small, but the favourable influence of the higher temperature on yields obtained with a relatively great space-velocity may once more be noticed.

Manganese.

Manganese, prepared from amalgam, was found to exhibit to a high degree the phenomenon of an apparently high initial activity, due to interaction of its nitride content with the hydrogen employed. After cessation of this transient formation of ammonia, the following results were obtained with a catalyst plug measuring about 3·5 cm. in length and 0·45 cm. in diameter:

TABLE XX.—*Catalyst: Manganese.*

Temperature, °C.	Pressure, atm.	S.V., 10^3 ×.	Per cent. NH_3.	S.T.Y.
600	159	3·6	2·35	0·06
650	159	3·6	3·4	0·06
650	169	89·0	1·73	1·1
702	179	18·0	3·12	0·40
708	177	32·0	2·90	0·67
694	169	54·0	2·25	0·87
700	166	72·0	1·91	0·99
692	170	89·0	1·55	0·99

Tungsten.

Finely divided tungsten as used in the manufacture of lamp filaments is inactive. In order to prepare tungsten in an active condition, the metal is heated in chlorine, with formation of the chloride, which is subsequently reduced in a current of ammonia.

On testing the activity of the preparation, a concentration of 2·4 per cent. of ammonia was obtained at 655° C. and 190 atmospheres pressure, with a gas current of about 2 litres per hour at room temperature and atmospheric pressure.

The volume of catalyst employed is not stated, but assuming this to be the same as for manganese, the result would correspond to a space-time-yield of 0·06 with a space-velocity of 3600.

The Synthesis of Ammonia at very high Temperatures.

The synthesis of ammonia by the action of induction sparks on a mixture of nitrogen and hydrogen has long been known. Deville[*] and Dixon[†] state that the gas mixture, when sparked in a eudiometer, undergoes a slow but complete conversion into ammonia, provided that the ammonia formed is continuously removed from the system by the action of acid. As might be expected, the elimination of ammonia from a system sparked in this way may also be effected by cooling instead of employing acids, so that complete transformation also takes place on immersing the sparking chamber in liquid air.

The recent discovery by Fowler and Gregory[‡] of ammonia in the sun lends additional interest to the nature of the equilibrium between nitrogen, hydrogen and ammonia at very high temperatures. Fowler and Gregory photographed the spectrum of ammonia, employing a 10-ft. concave grating, and found that a number of lines were obtained corresponding with group P in the ultraviolet of the solar spectrum, from which it would seem to be shown that many of the fainter solar lines are due to ammonia.

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[*] Deville, Cours de Chimie, 1846.

[†] Dixon, Proc. Manch. Lit. and Phil. Soc. (4), 1888, 1, 91.

[‡] Proc. R. Soc., 1918 (A), 94, 470; Phil. Trans., 1919 (A), 218, 351.

From a theoretical standpoint, the various equations, derived by integrating the reaction isochore by one of the methods already given, agree in indicating a reversal, at very high temperatures, in the sign of the temperature coefficient of the equilibrium ammonia content, this reversal being of such a nature that the equilibrium ammonia percentage should first sink with increasing temperature, then pass through a minimum, and finally increase once more. The degree of extrapolation required for applying these equations—which actually reproduce the experimentally observed results for the moderate temperatures corresponding to the region at which the physical measurements on which they are based were made—to extremely high temperatures, such as exist in an arc flame, is too great to render possible an exact and quantitative calculation of the ammonia equilibrium under such conditions. A reversal of the above nature would, however, appear to be indicated by each of the physical properties which are usually employed for calculating equilibrium, namely the temperature coefficient of the heat of formation and of the difference in specific heat of resultants and reactants.

The maximum concentration of ammonia obtainable by circulating a mixture of hydrogen and nitrogen through a tube containing a spark-gap, which was connected to an induction coil operated by an alternating current both with and without a contact-breaker, has been studied by Briner* and his collaborators, whose views on the mechanism of ammonia formation under these and similar conditions will be mentioned later.

The author,† in the course of an investigation on the relative efficiency of various types of spark, found that induction sparks as such exerted a comparatively feeble action on the synthesis, energetic formation of ammonia only taking place when the electrodes were brought sufficiently close together to transform the ordinary spark discharge into a small high-tension arc, accompanied by a visible and apparently continuous flame of high temperature.

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* Briner and Mettler, J. Chim. Phys., 1908, 6, 137; Briner and Kahn, *ibid.*, 1914, 12, 534.

† J. Chem. Soc., 1918, 113, 386.

Table XXI summarises the results obtained by varying the spark-gap from 10 mm. to 0·5 mm. with a constant rate of flow of 40 c.c. per hour, the small arc flame being formed between platinum electrodes in a capillary tube 0·65 mm. in diameter, through which the gas passed:

TABLE XXI.

Rate of flow of hydrogen-nitrogen mixture = 40 c.c. per hour.

Length of spark-gap in mm.	Nature of discharge.	Percentage of ammonia by volume in issuing gases.
10	Spark	< 0·1
5	Incipient flame	0·25
1·5	Arc flame	0·8
0·5	,,	1·1

The formation of ammonia by a larger high-tension arc,* formed by transforming single-phase 50-cycle alternating current, supplied at a maximum potential of 375 volts, by means of an oil-immersed static transformer having a step-up factor of 31·5, was also investigated.

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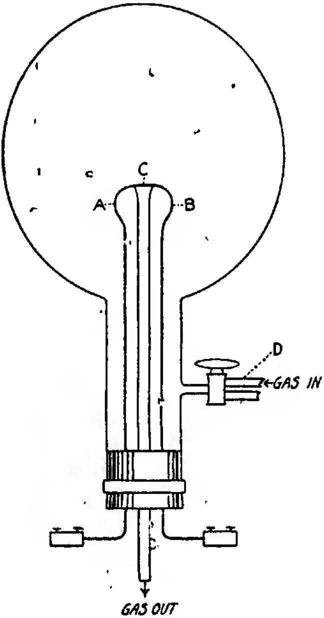
* Maxted, J. Chem. Soc., 1919, 115, 113.

The apparatus employed is shown in Fig. 9. The electrodes A and B were of platinum, and terminated in small spheres slightly more than 1 mm. in diameter.

FIG. 9.



C is a thick-walled capillary silica tube, its upper end being opened out and flattened so as to form a slit approximately 4 mm. long and 1·5 mm. wide. The silica wall bounding the ends of this was ground away, and the electrodes rested in the depression thus formed at each end of the silica slit, the lower part of the tube being circular in section and about 1·5 mm. in internal diameter.

The arc was enclosed in a large inverted flask provided with a side tube and a three-way tap D, for preliminary exhaustion and subsequent admission of the gas to be subjected to the action of the arc, this gas passing normally into the flask at D and leaving the system by way of the silica tube already described.

For these measurements the current employed for arc-formation was limited by the interposition of an adjustable resistance on the low-tension side of the transformer.

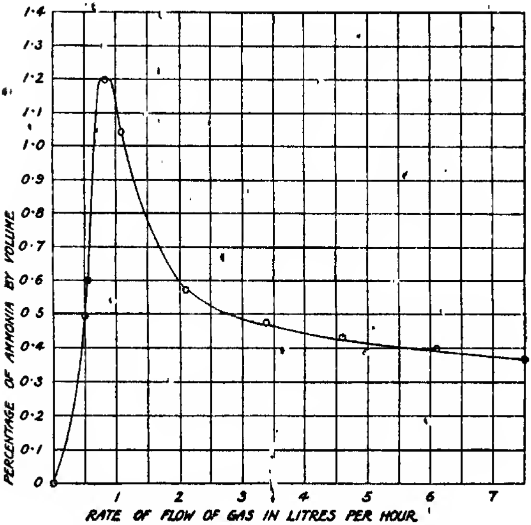
The platinum electrodes became quickly white-hot and the arc flame burned steadily across the slit, and was, to a certain degree, drawn into the tube by the current of gas. Sufficient cooling for the recovering of the greater portion of the ammonia formed and for the prevention of the fusion of the silica tube was obtained without water-cooling, provided that a thick-walled silica capillary was used and that the arc employed was not too large.

Samples of gas, taken at various rates, were analysed by passage through N/10-acid, and in some cases by allowing a small volume to pass through Nessler's solution, practically identical results being obtained by each method of analysis.

The quantity of ammonia observed was influenced necessarily not only by the temperature of the arc, but also by heating and cooling factors. With very slow currents of gas, heating to arc temperature occurs satisfactorily, but the ammonia formed undergoes considerable decomposition owing to the slowness with which it leaves the region of maximum temperature. Passage of the gas too quickly through the arc results in imperfect heating, such rapid passage, however, involving rapid cooling, and consequently a more complete retention of the ammonia formed.

It will be seen from Fig. 10, which represents in a graphical form the results obtained, that the concentration of the ammonia recovered at ordinary temperature first of all rises rapidly with increasing velocity of passage, then passes a maximum value, the percentage of ammonia subsequently falling gradually with still greater velocity of passage. This form of the concentration-velocity curve is a necessary result of the nature of the heating and cooling factors discussed above.

FIG. 10.



The issuing gas, of course, had a strong odour of ammonia at all the rates of flow studied, and the percentages obtained were of the same order of magnitude as those previously observed with small arcs not produced directly by a high-tension current of the usual sinusoidal wave-form. For this series of experiments 0·04 ampère at a potential of 3250 volts was taken for arc-formation.

As an alternative to employing an arc flame as the source of high temperature, ammonia may also be formed by heating a mixture of nitrogen and hydrogen to the temperature of the oxy-hydrogen flame, this heating being followed by rapid cooling in order to retain in an undecomposed condition the ammonia formed at flame temperature. Table XXII records some results obtained by the author* by injecting a gas mixture containing 33 per cent. of nitrogen and 67 per cent. of hydrogen into an oxy-hydrogen flame burning under water, or in some cases under dilute sulphuric acid :

TABLE XXII.

No. of expt.	Velocity in litres per hour of gases passed into reaction chamber.			Observed percentage of ammonia by volume in mixture of nitrogen and hydrogen.	Estimated temperature of flame, ° abs.
	N_2.	H_2.	O_2.		
1	60	220	20	0·00235	1280
2	60	260	40	0·005	1500
3	60	360	90	0·013	1830
4	30	270	90	0·018	2120
5	20	240	90	0·0205	2260
6	20	300	120	0·037	2350
7	20	460	200	0·07	2470
8	10	430	200	0·112	2580

The apparatus, which is shown in Fig. 11, consisted of a silica tube 6·5 mm. in diameter and 7·5 cm.

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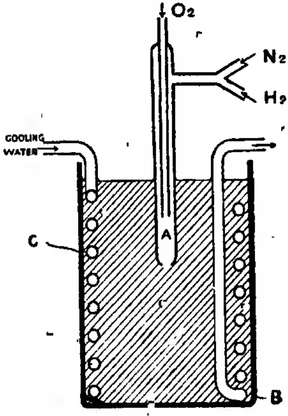
* J. Chem. Soc., 1918, 113, 168; J. Soc. Chem. Ind., 1918, 37, 105 T.

long, completely immersed, in about 900 c.c. of distilled water contained in a glass vessel, fitted with a glass cooling coil, through which a rapid current of water was passed. Into the quartz reaction vessel, nitrogen, hydrogen and oxygen, at rates determined by velocity meters, were injected and ignited, the flame passing out at the open end of the reaction chamber and through the water, by the action of which the ammonia, recovered from the flame by sudden cooling, was retained. In most cases the water was acidulated with sulphuric acid in order to ensure complete absorption of the ammonia.

FIG. 11.



It is probable that some of the ammonia obtained at high temperatures, particularly from arc flames, is formed in a manner not strictly comparable with the synthesis as it occurs at moderate temperatures in the presence of catalysts. An analogous example is to be found in the work of Haber and Koenig,* who obtained nitric oxide in proportions considerably in excess of the equilibrium percentage, calculated on purely thermal grounds, by the action of a relatively "cold" arc burning in a mixture of nitrogen and oxygen. Such secondary formation of substances in arc reactions is generally ascribed to the ionising effect of forces of an electrical nature—a view which was put forward by Perman in 1905.* Briner and Baerfuss† consider that the function of the high temperature is to dissociate the molecules of nitrogen and hydrogen into atoms, which diffuse as such into a zone of low temperature and there unite to form ammonia. In support of this view, experiments are given in which the yield of ammonia was found to be enhanced by reducing the pressure to 100 mm., and also in certain cases by increasing the nitrogen content of the mixture sparked. The mechanism suggested would not, on the other hand, account for the presence of ammonia in the sun.

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* Z. f. Elektrochem., 1907, 13, 725; 1908, 14, 689.

In no work published up to the present has the temperature of formation been sufficiently accurately measured, nor has this been sufficiently uniform and constant, to render possible a satisfactory investigation of the degree of conformity or non-conformity of the reaction to the law of mass action, and to the results which would seem to be indicated on thermodynamical grounds from purely thermal data. With a view to examining this point, the author has recently investigated the concentration of ammonia produced by an electrically heated tungsten spiral glowing in a mixture of nitrogen and hydrogen, the temperature being measured optically by means of a polarising type of pyrometer, with a correction for the absence of black body radiation. Even at 2500° and slightly over, the yield of ammonia was very small. The walls of the reaction vessel became quickly blackened by volatilisation of the tungsten, and special precautions were necessary in order to obtain a reliable record of temperature. At very high temperatures tungsten spirals become unable to support their own weight and straight wires have to be used, but in any case the temperature at which appreciable concentrations of ammonia can be obtained would appear to be higher than can be successfully realised with the aid of a tungsten filament or tube. It may be noted, further, as will be seen on referring to the results obtained in a high-tension arc (see Fig. 10), that the velocity of ammonia formation at high temperatures is strikingly low in comparison with the formation of, for instance, nitric oxide.

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* Proc. R. Soc., 1905, 76, 167.

† Helv. Chim. Acta., 1919, 2, 95, 162.

In addition to its synthesis in arc and other flames, ammonia may also be formed by the silent discharge; thus M. Berthelot[*] was able to obtain a concentration of about 3 per cent. of ammonia by volume by this means. Somewhat similar results were obtained by Donkin[†] and by Le Blanc and Davies.[‡]

Briner and Kahn,[§] who studied the effect of diminished pressures on the maximum concentration of ammonia obtainable, give the results summarised in Table XXIII. It will be seen that a higher maximum concentration was obtained at a pressure of 100 mm. than at atmospheric pressure, this being analogous to Briner and Kahn's results with spark discharge.

In order to investigate the influence of the velocity of gas passage on the concentration of ammonia obtained by the silent discharge, the author caused a 1 : 3 nitrogen-hydrogen mixture, previously freed from oxygen and moisture by sodium hydrosulphite and phosphorus pentoxide respectively, to pass at various known rates through a discharge tube of the usual annular form, this space being of small dimen-

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[*] Bull. Soc. Chim., 1876, 26, 101.

[†] Proc. R. Soc., 1873, 21, 281.

[‡] Z. f. Elektrochem., 1908, 14, 361.

[§] J. Chim. Phys., 1914, 12, 534.

TABLE XXIII.

Initial pressure of system, mm. Hg.	Final pressure of system.	Maximum percentage of ammonia by volume.
696·15	685·35	1·55
463·15	458·35	1·08
251·2	248·7	1·0
149·95	148·9	0·7
100·5	97·7	2·35

sions in order to obtain an intensive discharge. The results obtained are given in Table XXIV. The annular space possessed a mean diameter of 3 mm. and a length of 7·5 cm., the breadth of the annulus, which was formed by two closely fitting glass tubes, being 0·25 mm. The apparatus was connected with an induction coil, which was operated directly from the laboratory 220-volt main, a lamp resistance, sufficient to reduce the primary current to 3·5 ampères, being included in the circuit. The ammonia was estimated by means of Nessler's solution.

TABLE XXIV.

Rate of gas flow in c.c. per hour.	Percentage of ammonia in issuing gas.
920	0·03
530	0·06
176	0·15
38	0·53
14·7	0·90
4·2	2·44
2·1	3·00
1·44	4·1

It is worthy of note that Strutt's active nitrogen, which readily forms nitrides when allowed to act on metals such as mercury, does not unite spontaneously with hydrogen with formation of ammonia.

CHAPTER III.

THE NITRIDES.

General Methods of Preparation.

THE general methods of nitride formation may be classified in the following categories:

(1) Direct union of the elements.

(2) Interaction of the nitride-forming element with ammonia.

(3) Action of ammonia on an oxide or salt.

(4) Formation by double decomposition with other nitrides.

(5) Formation by decomposition of an amide or imide.

Formation of Nitrides by Direct Union with Elementary Nitrogen.

The various elements which are capable of forming nitrides directly do not, in general, absorb nitrogen with measurable velocity unless they are more or less strongly heated in the gas. Lithium, which readily combines with nitrogen even at room temperature,* is, however, a remarkable exception to the general rule.

The following elements form nitrides when heated in nitrogen:

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* Deslandres, C.R., 1895, 121, 886.

Lithium.
Calcium.
Strontium.
Barium.
Magnesium.
Boron.
Aluminium.
Various rare earths.
Titanium.
Zirconium.
Cerium.
Thorium.
Silicon.
Vanadium.
Niobium.
Tantalum.
Chromium.
Uranium.
Manganese.

It may be necessary in certain instances to prepare the element in a more easily reactive condition than when in the compact state—for instance by forming an amalgam and distilling off the mercury, the finely divided element thus produced being subjected to the action of nitrogen either during or subsequent to this distillation. This method of preparation has been successfully applied *inter alia* to chromium* and manganese.†

In cases where the reaction with nitrogen only takes place at a very high temperature, the element may often with advantage be employed in a nascent condition by heating its oxide, or a salt such as the chloride, in nitrogen with the addition of a reducing body. This principle finds application in the formation of many nitrides at the temperature of the electric furnace, the method being especially applicable to boron, aluminium, silicon and uranium.

The reducing agent most frequently employed is carbon. This, however, is not applicable for cases where it reacts with the nitride or nitride-forming element with formation of a cyanide or similar compound. With the alkaline earths, this participation of carbon in the reaction leads to the complete suppression of the nitride:

$$BaO + 3C + N_2 = Ba(CN)_2 + CO$$
$$CaO + 2C + N_2 = CaN.CN + CO.$$

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* Ferée, Bull. Soc. Chim. (3), 1901, 25, 618.
† Prelinger, Monatsh., 1894, 15, 391.

In the latter instance, the temperature at which reaction with nitrogen takes place is lower than the reduction temperature of calcium oxide, so that the reaction is carried out in two stages, during the first of which the metal, obtained by reduction from its oxide, unites with carbon, the carbide thus produced being subsequently heated to a lower temperature in nitrogen.

It is obvious that the direct combination with nitrogen of an element which is readily reducible from its oxides or salts should constitute a solution of the nitrogen-fixation problem, and it is, from this point of view, unfortunate that the elements which form nitrides directly are without exception only capable of being reduced from their oxides at comparatively high temperatures. As an example of this, of the three elements, manganese, chromium and iron, both manganese and chromium unite directly with nitrogen but are only reduced from their oxides at a white heat, while iron, which is readily obtained by the action of reducing gases on its oxide even at 400° C., does not form a nitride directly.

In order to prepare moderate quantities of a nitride by direct union with nitrogen, the most usual procedure consists in placing the element in an iron or other boat, which is inserted in a porcelain combustion tube and heated to the required temperature by means of a resistance furnace. In certain cases a glass tube heated in a combustion furnace may be used, the apparatus depending entirely on the temperature necessary to induce the reaction, and on the ease with which the containing vessels are attacked by the nitride-forming element at this temperature. An ingenious method which was employed by many of the earlier investigators (Berzelius, St. Claire Deville, Wöhler, etc.) consists in placing the element in a crucible, which was in its turn placed in a larger crucible containing carbon, by the action of which penetration of oxygen to the inner crucible was prevented, while the atmospheric nitrogen required for nitride formation passed freely through. The separate preparation of oxygen-free nitrogen was thus avoided.

Small quantities of many nitrides, some of which are not capable of being prepared by other methods, may be obtained by a thermal method worked out by Franz Fischer and his pupils.* According to this method of preparation, an arc is established between poles of the nitride-forming element in a mixture containing liquid nitrogen. A mixture of the vapour of the required element and nitrogen is raised locally to a high temperature, and quickly cooled by the excess of liquid surrounding the arc. In order to increase the rate of disintegration of the cathode, the nitrogen employed was mixed with nine times its volume of argon, which was prepared by the action of air on calcium carbide, the mixture being condensed, as required, by means of liquid air.

The apparatus is shown diagrammatically in Fig. 12. It consists of a glass tube A, containing a fused-in platinum connection B, on which is mounted a cathode of the metal the nitride of which it is desired to obtain. The moveable anode is shown at C, the distance between anode and cathode being regulated by a rotating head D, which engages in a screw at the upper end of the rod E, carrying the anode, entrance of air being guarded against by means of a mercury seal. F and G are side tubes for collecting the nitride formed, by tipping the reaction tube on a ground-in joint in the plane of the paper.

In many instances it was found sufficient to employ a cathode of the nitride-forming metal, the anode being of silver. In order to carry out an experiment, the reaction tube was evacuated and connected to a source of the nitrogen-argon mixture. Sufficient of this to cover both electrodes was condensed by

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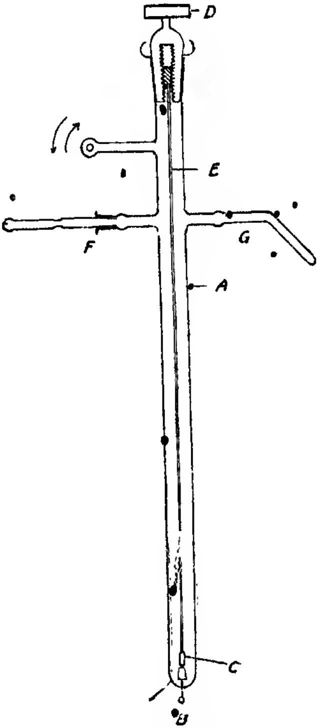
* Fischer and Iliovici, Ber., 1908, **41**, 3802, 4449; Fischer and Schröter, *ibid.*, 1910, **43**, 1465.

FIG. 12.



immersing the reaction tube in liquid air, which was further cooled by being allowed to evaporate into a vacuum in a special attachment.

The arc was next started between the electrodes and allowed to burn during the entire experiment, at the end of which the cooling bath of liquid air was removed and the liquid nitrogen-argon mixture allowed to evaporate into a gas-holder, the nitride formed being thus left in a dry condition in the reaction vessel, from which it was transferred into the side tubes F and G.

Working in this way, small quantities were obtained of the nitrides of sodium, potassium, rubidium, copper, zinc, cadmium, mercury, indium, thallium, tin, lead, arsenic, antimony, bismuth and manganese. Many of these bodies were highly explosive, and only in a few cases was the product sufficiently pure (by reason of the presence of excess of metal) or in sufficient quantity for quantitative analysis, the presence of nitride being detected by dissolving in acid and testing for ammonia by means of Nessler's solution, or alternatively by heating the nitride in a vacuum and examining spectroscopically the gas evolved.

A further method of preparing nitrides by the direct combination of the elements consists in employing the nitrogen in the active form obtained by electrical discharge under diminished pressure. Details of this method are given in a later chapter.

Preparation of Nitrides by the Action of Ammonia on the Element.

In certain instances, in which an element does not react with nitrogen directly, a nitride may be obtained by employing ammonia in place of nitrogen itself, in which case, provided that the preparation is carried out at a relatively high temperature, the nitrogen is rendered available in a nascent condition. An example of this method is to be found in the preparation of iron nitride. Iron does not combine with free nitrogen even when heated at a high pressure in the gas, but on passing ammonia over the heated metal, the former is decomposed into nitrogen and hydrogen, and a portion of the nitrogen thus produced combines with the iron to form nitride.

Frequently the nitrides, prepared by this method, decompose into their elements when heated in nitrogen or hydrogen to a temperature slightly higher than that at which they are formed, or even to this temperature itself, while they are found to be stable at a considerably higher temperature, provided that they are surrounded by undecomposed ammonia. In the case of iron, which forms a typical example of this class, a maximum fixation of nitrogen is obtained at about 460°–480° C. under ordinary conditions. The nitride begins to decompose in nitrogen or hydrogen at about 500° C., and decomposition takes place rapidly and completely at 600°. Provided that a sufficiently rapid current of ammonia is employed (by which means decomposition is reduced to a minimum and an atmosphere of comparatively pure ammonia produced), iron nitride may readily be prepared at 700°–800° C.

As a consequence of the decomposition of the nitrides of this class at or near the temperature of formation, the product, even under optimum conditions, contains a certain proportion of the free element, the composition being determined by the relative velocities of decomposition and formation. For this reason, the formulæ obtained by direct analysis of such nitrides are usually not to be taken as representative of their true constitution.

In order to produce a nitride containing a maximum percentage of nitrogen, the surface of the metal may, for instance, in the preparation of zinc nitride, be advantageously made as large as possible by employing a fine powder, and the current of ammonia should be rapid. This applies also to the other nitrides of this class.

It is found in some cases that, while an element reacts with nitrogen in the free state, a greater percentage of this is fixed by heating in ammonia. Thus finely divided manganese when heated in nitrogen forms a body possessing a composition approximating to Mn_5N_2, while with ammonia the nitride formed approximates to Mn_3N_2.

The apparatus employed for this method is usually simple, the element being contained in a boat, which is placed in a porcelain or glass tube and heated to the required temperature by means of a gas or electric tube furnace.

Preparation of Nitrides by the Action of Ammonia on an Oxide or Salt.

It is possible in certain cases to prepare nitrides, which are not obtained by the action of nitrogen or of ammonia on the element, by allowing both the nitride-forming element itself and nitrogen to react in a nascent condition, this being usually effected by passing a current of ammonia over a heated oxide or salt. As examples of the method copper or mercury nitride may be cited. In the former case the reaction takes place at 270°–310° C. according to the equation—

$$3Cu_2O + 2NH_3 = 2Cu_3N + 3H_2O,$$

but the product, as is the case with many instances of this and similar modes of preparation, always contains unchanged metal or oxide—indeed, the oxygen content of the impure mercuric nitride led to the view that the product, instead of being a true nitride, contained oxygen as an integral part of its constitution.

With boron, the method renders unnecessary the rather inconvenient preparation of the free element, the nitride being readily formed by the action of ammonia on boron trioxide at 800° C.

Reactions of a similar nature also take place in some cases at room temperature and in aqueous solution. Thus on dissolving silver oxide in concentrated ammonia solution and allowing the liquid to stand, silver nitride is found to separate out.

In place of an oxide, a salt, such as the chloride. may sometimes be employed. An example of this may be found in the preparation of iron nitride, which is obtained with equal facility by the action of ammonia on ferrous chloride, on iron oxide, or on the metal itself. Vanadium, niobium and tantalum nitrides may also be made from their chlorides or oxychlorides in the same way.

Of gaseous nitrogen compounds other than ammonia, cyanogen has been used for the formation of beryllium nitride.

Nitride Formation by Double Decomposition.

The preparation of nitrides by double decomposition has not been worked out to any great extent. Smits* states that copper nitride may be obtained in this way by heating copper oxide with magnesium nitride, but the product is very impure.

It may also be noted that iron nitride is formed during the preparation of lithium nitride or of a nitride of an alkaline earth in an iron boat.

Formation of Nitrides by the Decomposition of Amides or Imides.

In cases where the element forms an amide, it is frequently found that this body, on being heated, passes into a nitride either with or without the intermediate production of an imide. The behaviour of arsenamide is typical of this method of nitride formation. On being heated to 60° C. the amide changes to imide; a molecule of ammonia being split off, and on further heating to 250° C. the imide passes in turn to nitride:

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* Rec. Trav. Chim. Pays-Bas., 1896, 15, 135.

$$(a)\ 2As(NH_2)_3 = As_2(NH)_3 + 3NH_3$$
$$(b)\ As_2(NH)_3 = 2AsN + NH_3.$$

Similarly zinc nitride is formed by heating zinc amide to 260° C., and barium nitride by heating the amide of this metal to 430° C., although in the latter case the nitride is more easily prepared by the direct interaction of the elements.

In some instances the amide itself is unstable even at low temperatures, and the nitride is produced under conditions such that the amide would be expected. This applies particularly to reactions between potassamide and salts of other metals in liquid ammonia solution. As an example of this effect, the double decomposition between potassamide and mercuric iodide or bismuth bromide may be instanced. The reactions in question were found by Franklin to take place according to the equations—

$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$$
$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3.$$

It was stated by Thénard and Gay Lussac that a nitride of sodium or potassium could be obtained by heating the corresponding amide, but the observation, in the light of more recent work, would appear to be erroneous.

General Properties of Nitrides.

The normal nitrides may be regarded as ammonia, in which the hydrogen atoms have been completely replaced by another element.

Accordingly, the normal formulæ for nitrides of the various elements, which exhibit in these compounds valencies from 1 to 6, will be as follows:

TABLE XXV.

Valency of element.	Normal formula of nitride.	Examples.
Monovalent	M_3N	Li_3N, Cu_3N, Ag_3N, Au_3N.
Divalent .	M_3N_2	Ca_3N_2, Ba_3N_2, Sr_3N_2.
Trivalent .	MN	BN, AlN, AsN, SbN, BiN.
Tetravalent	M_3N_4	Si_3N_4, Ti_3N_4, Th_3N_4, U_3N_4.
Pentavalent	M_3N_5	Nb_3N_5, Ta_3N_5, P_3N_5.

From their relationship to ammonia the nitrides are easily resolved into this body by the action of acids or alkalies; indeed the latter especially of these two reactions may be regarded as characteristic of nitrides as a class. In some cases the nitrides are insoluble both in acids and in aqueous alkalies, and fusion with solid caustic potash or soda is necessary in order to obtain the ammonia reaction. In other instances the nitride reacts even with water in the cold, and indeed the reaction may be sufficiently vigorous to cause incandescence if only a small quantity of water is used. This, for instance, is the case with cerium nitride. An example of the opposite extreme, namely a high degree of indifference to the action of aqueous acids or alkalies, is to be found in silicon nitride, which may even be purified from free silicon by being treated with warm aqueous caustic potash.

Usually the nitrides react with steam, which may need to be superheated, also in some instances with hydrogen, ammonia being formed in each case. The latter reaction may, as is the case, for instance, with cerium, involve the simultaneous formation of a hydride, the change being often reversible.

When oxidised, the nitrides, in almost every instance, pass into the oxide of the element and free nitrogen. The formation of oxides of nitrogen has, however, been noted during the oxidation of boron nitride by easily reducible metallic oxides.

In the following chapter a short systematic account is given of the various nitrides, these being dealt with in the order of the periodic system.

CHAPTER IV.

NITRIDES OF GROUPS I, II AND III OF THE PERIODIC SYSTEM.

Nitrides of the Alkali Metals.

LITHIUM differs from the other alkali metals by the readiness with which it combines directly with nitrogen. Ouvrard* heated metallic lithium, contained in an iron boat, slowly to redness in a current of nitrogen, when the metal became incandescent and a nitride was formed corresponding to the formula Li_3N. This was confirmed by Guntz.† Deslandres‡ states that the combination of lithium with nitrogen also takes place in the cold, and is sufficiently complete to cause the spectroscopic disappearance of the nitrogen bands. The absorption of nitrogen is prevented by the film of oxide with which the metal is usually covered.

When prepared in an iron or nickel boat, lithium nitride usually contains traces of these metals, which separate out as ferric hydroxide and as Ni_2O_3 respectively on dissolving the mass in water. Boats of platinum or silver cannot be employed (*cf.* "Preparation of Nitrides of the Alkaline Earths") since they dissolve in the molten lithium during the reaction.

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* C.R., 1892, 114, 120.
† C.R., 1895, 120, 777.
‡ C.R., 1895, 121, 886.

The nitride is described as a spongy black mass which readily reacts with water with formation of ammonia and of lithium hydroxide. On being heated in hydrogen, lithium nitride passes into hydride, but the reverse reaction is complicated by the dissociation of lithium hydride by heat alone.

Sodium, potassium, rubidium and cæsium do not form nitrides when heated in nitrogen under ordinary conditions. Gay Lussac and Thénard described a black nitride of sodium prepared by heating sodamide; but Titherley* was unable to obtain either this or the corresponding potassium compound.

Fischer and Schröter† obtained sodium, potassium or rubidium nitride, mixed with the free element, by the action of an arc burning between poles of the metal in question in a liquid nitrogen-argon mixture. The product was black in the case of sodium, blue for potassium or rubidium. On heating gently nitrogen was evolved explosively. These nitrides dissolved readily in water with production of ammonia. After decomposition by heating, the product was found to give no reaction with Nessler's solution.

Copper Nitride (Cu_3N).

The preparation of cuprous nitride by the action of ammonia on cupric oxide was described by Schrötter in 1841.‡ Schrötter states that a suitable temperature for formation is about 250°C., and, as is usual with nitrides prepared by this method, the product always contains free oxide or metal. The rate of formation is slow, a period of 120 hours being necessary for the preparation of about 20 grm. of the nitride by heating the cupric oxide in a glass tube in a current of ammonia. Three products prepared in this way were found to contain 7·14, 7·09 and 7·2 per cent. of nitrogen respectively, the remainder being copper, with the exception of about 0·17 per cent. of hydrogen, which was probably present in the occluded condition. Beilby and Henderson* state that no nitride is formed unless the ammonia is present in large excess, the maximum percentage of nitrogen fixed in their experiments being 4·5. Güntz and Bassett prepared the nitride from cuprous instead of cupric oxide.† The reaction begins at 270° C. and is rapid at 310°, but the nitride begins to decompose at the temperature of production. The products obtained contained about 6 per cent. of nitrogen, and it was found possible to remove the free copper by treatment with a solution of ammonia and ammonium carbonate.

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* J. Chem. Soc., 1894, 65, 504.

† Ber., 1910, 43, 1465.

‡ Annalen, 1841, 37, 131.

The nitride thus purified contained about 6·8 per cent. of nitrogen. The formula Cu_3N, corresponding to lithium nitride, requires 6·86 per cent.

Copper nitride may also be obtained by the interaction of copper oxide with magnesium nitride,‡ but the product is very impure. Similarly, on heating cuprous or cupric chloride with lithium nitride a reaction takes place. This is, however, so violent that copper only is obtained, the nitride being decomposed by the high temperature.

Cuprous nitride is a greenish-black powder, which decomposes into its elements on being heated to 300° C. Schrötter states that the decomposition is accompanied by a red glow. It dissolves in acids, forming ammonium salts and cuprous salts:

$$2Cu_3N + 8HCl = 3Cu_2Cl_2 + 2NH_4Cl.$$

Cuprous nitride is decomposed normally, althougn not very quickly, by boiling caustic soda solution, with evolution of ammonia:

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* Trans. Chem. Soc., 1901, 71, 1252.

† Bull. Soc. Chim. (3), 1906, 35, 201.

‡ Smits, Rec. Trav. Chim. Pay-Bas., 1896, 15, 135.

$$2Cu_3N + 3H_2O = 3Cu_2O + 2NH_3.$$

Silver Nitride. (*Ag_3N*).

This body was first prepared by Berthollet[*] by the action of aqueous ammonia on silver oxide. F. Raschig,[†] who examined the subject in greater detail, showed that the nitride possesses the normal formula Ag_3N.

In order to prepare the body in a pure condition, each gram of silver nitrate is allowed to react with 2 c.c. of concentrated ammonia solution, containing about 25 per cent. of ammonia. The resulting solution of silver oxide in excess of ammonia is allowed to stand from 16 to 20 hours in the dark, when a crystalline precipitate of silver nitride separates out. The precipitation of silver nitride may also be effected by heating the solution gently on the water-bath, in which case, however, the product must not, on account of its explosive nature, be disturbed until cold, or the nitride may be separated by adding to the ammoniacal solution about ten times its volume of alcohol. The precipitate which forms is in each case of a light colour, which, however, quickly becomes black on standing. When fresh it has a composition corresponding to the formula Ag_3N, but it undergoes a slow and spontaneous decomposition into silver and nitrogen, and for this reason specimens of the nitride usually contain free silver. It explodes extremely easily and with great violence, especially when dry.

When treated with aqueous hydrochloric acid the nitride passes in the normal way into ammonium chloride and silver chloride, but the reaction is hampered by the insolubility of the latter body. With nitric acid it reacts similarly but completely.

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[*] Crell. Ann., 1788, 2, 390.

[†] Annalen, 1886, 233, 93.

On being treated with a solution of potassium cyanide the following reaction takes place:

$$NAg_3 + 3KCN + 3H_2O = NH_3 + 3KOH + 3AgCN.$$

Nitrides of Gold (*Au_3N and Au_3N_2*).

Aurous nitride (Au_3N), may be prepared by adding concentrated aqueous ammonia to aurous oxide (Au_2O). On allowing the mixture to stand for several days a black explosive powder having the composition $Au_3N.NH_3$ is formed, and on boiling the suspension of this body in water for a quarter of an hour the substance loses ammonia and passes into the free nitride.*

By a similar reaction between auroauric oxide and ammonia Raschig obtained a nitride corresponding to Au_3N_2, according to the equation:

$$3AuO + 2NH_3 = Au_3N_2 + 3H_2O.$$

Nitrides of the Alkaline Earths (*Ca_3N_2, Sr_3N_2, Ba_3N_2*).

The alkaline earth-metals, calcium, barium and strontium, all combine readily with nitrogen when heated in the gas, forming nitrides of the general formula M_3N_2. Maquenne† obtained these bodies by heating an amalgam of the metal in question in an atmosphere of nitrogen. The amalgam was raised slowly to dull redness, the mercury being driven off during this process. The temperature was then increased for a short time to bright redness and the nitride allowed to cool in the gas. The preparation should be carried out in an iron or nickel boat, since platinum is attacked (*cf.* lithium); but in any case, the material of the boat is found to be present in the product, which also contains free alkaline-earth metal. After allowing for these impurities, the latter of these being estimated by measuring the volume of hydrogen evolved on solution in water, the composition of the nitride was found in each case to correspond to that given above. The amalgams used were prepared by the electrolysis of concentrated aqueous solutions of the alkaline earth-chlorides with a mercury cathode, the yields, however, not being high.

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* Raschig, Annalen, 1886, **235**, 348.

† C.R., 1892, **114**, 25.

Instead of employing the free metals, or an amalgam of these, Gautier[*] has shown that a convenient method of preparation consists in heating an alloy of calcium, strontium or barium with cadmium in a current of nitrogen. Absorption begins to take place at about 600° C., and the nitrides are quite stable at 1000°.

Nitrides may also be formed by heating in nitrogen a mixture of an oxide or salt of the alkaline earth-element and a metal, such as magnesium, which is capable of reacting with the oxide or salt employed, with production of the element required. Maquenne[†] heated in nitrogen a mixture of magnesium with calcium, strontium or barium oxide, with rapid formation of nitrides of the latter elements. The product is from its method of preparation mixed with magnesia. Limb[‡] states that barium nitride may be obtained by heating barium fluoride to a moderate temperature in nitrogen in the presence of sodium. Barium hydride[§] also reacts with nitrogen when heated to a red heat in a current of the gas with formation of nitride.

A further method of preparation[‖] consists in heating, for instance, barium amide *in vacuo* to about 430° C., when ammonia is given off and nitride remains. The decomposition

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[*] C.R., 1902, 134, 1108.

[†] C.R., 1895, 121, 1147.

[‡] Thesis, Essais sur la preparation du barium metallique, Paris, 1895.

[§] Guntz, C.R., 1901, 132, 913.

[‖] Guntz and Mentrel, Bull. Soc. Chim. (3), 1903, 29, 578

$$3Ba(NH_2)_2 \rightleftarrows Ba_3N_2 + 4NH_3$$

is reversible. The amide is easily prepared by heating barium in ammonia to a temperature of 300° to 380° C.

The nitrides of the alkaline-earth metals are brown or yellow bodies which are very unstable in damp air. Barium nitride has been obtained in the form of yellow needles. They react readily with water, with production of ammonia, and dissolve in dilute acids with considerable violence with formation of ammonia salts, no evolution of gas taking place provided that the nitride is pure.

When heated in carbon monoxide barium nitride reacts with the gas, forming cyanide:

$$Ba_3N_2 + 2CO = Ba(CN)_2 + 2BaO$$

The reaction is of interest in connection with the fixation of nitrogen as cyanide by heating a mixture of barium oxide and carbon in nitrogen, but it may also be noted that barium forms a carbide directly.* The molecular heat of formation of barium nitride is about 99,600 calories.

Beryllium Nitride.

Metallic beryllium is stated to be unchanged when heated either in ammonia or in nitrogen. Vournasos† has prepared beryllium nitride by acting on beryllium with cyanogen at 800° C.

Magnesium Nitride (Mg_3N_2).

St. Claire Deville and Caron‡ stated in 1857 that when magnesium was distilled in air the distilled product was sometimes covered with small, colourless, transparent needles, which were destroyed quickly by the action of moisture, with formation of ammonia and magnesia. Brieglieb and Geuther§ prepared the nitride by heating magnesium filings in a porcelain boat in a wind furnace, when nitrogen was vigorously absorbed. The employment of a high temperature was found by Merz* to be unnecessary and even undesirable, since combination readily takes place by heating magnesium in a glass tube by means of a bunsen flame. The glass is blackened during the operation, owing to the liberation of silicon. The nitride may also be formed at a somewhat lower temperature by the action of ammonia in place of free nitrogen on magnesium, but in any case the gas employed must be dry and free from oxygen.

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* Maquenne, C.R., 1892, **114**, 361.
† Bull. Soc. Chim. (4), 1917, **21**, 282.
‡ C.R., 1857, **44**, 394.
§ Annalen, 1862, **123**, 228.

Magnesium nitride, as usually prepared, is a greenish-yellow mass, which smells of ammonia on being allowed to stand in air. It reacts violently with water and with dilute acids, with formation of the normal products. It is to be noted that magnesium nitride is scarcely attacked by concentrated sulphuric acid.

Briegleb and Geuther report that when magnesium nitride is heated in carbon monoxide or dioxide the following changes occur:

$$6CO_2 + 4Mg_3N_2 = 12MgO + 3C_2N_2 + N_2$$
$$3CO + Mg_3N_2 = 3MgO + C_2N_2 + C$$

These reactions have recently been questioned by Fichter and Schoelly,† who passed a current of carbon monoxide and carbon dioxide respectively over magnesium nitride at 1250° C. and observed no formation of cyanogen, the reaction taking place according to the equations—

$$Mg_3N_2 + 3CO_2 = 3MgO + 3CO + N_2$$
$$Mg_3N_2 + 3CO = 3MgO + N_2 + 3C$$

Carbon monoxide did not react at 750° C., and even at higher temperatures decomposes the nitride less readily than carbon dioxide.

The composition of magnesium nitride is readily determined by solution in dilute hydrochloric acid and estimation of the ammonia and magnesium chloride formed.

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* Ber., 1891, 24, 3940.

† Helv. Chim. Acta., 1920, 3, 298.

Zinc Nitride (Zn_3N_2).

White and Kirschbraun* prepared zinc nitride by passing ammonia over zinc powder at 600° C. The black body thus obtained was found to decompose slowly into its elements at the temperature used for its formation, and for this reason the product did not consist of pure nitride, but possessed a composition depending on the relative velocity of its formation from zinc and ammonia and that of the loss of nitrogen by decomposition. Many examples of this phenomenon in similar methods of preparation of nitrides occur (*cf.* copper, iron, etc.). In order to prepare products containing a maximum percentage of fixed nitrogen the surface of the metal was increased by employing fine powder, when preparations containing up to 10·6 per cent. of nitrogen were obtained. The formula Zn_3N_2 requires 12·5 per cent. of nitrogen.

Zinc nitride has also been prepared by Frankland† by heating zinc amide to 200° C.:

$$3Zn\ (NH_2)_2 = Zn_3N_2 + 4NH_3$$

The zinc amide was prepared by the action of ammonia on zinc ethyl.

White and Kirschbraun's product consisted of a black powder, which was readily decomposed by dilute acids with formation of ammonium salts and zinc salts. The colour of Frankland's preparation is described as green, but otherwise its properties seem to agree with the nitride obtained by the action of ammonia on zinc. Zinc nitride is stated by Frankland to be vigorously decomposed by water with formation of ammonia and zinc oxide.

J. Am. Chem. Soc., 1906, 28, 1343.
Phil. Mag. (4), 1858, 15, 149.

Under certain conditions zinc appears to combine directly with nitrogen; thus Arons[*] reports the formation of a small quantity of nitride by the action of an arc between zinc poles in an atmosphere of nitrogen.

It may be noticed that Fischer and Schröter observed the formation of zinc nitride by the thermal method, already described in detail. The product, which was mixed with free zinc, contained 6·5 per cent. of nitrogen. It appears to differ, however, from the nitride prepared by other methods by the ease with which it is decomposed into its elements by the action of heat.

Cadmium Nitride.

Cadmium nitride appears to have been prepared only by the thermal method, to which reference has frequently been made. The product consisted of a black powder, which exploded, although not very violently, on attempting to obtain a sample for analysis, covering the inside of the silica tube with a cadmium mirror and evolving nitrogen. In a further experiment a small sample was successfully extracted, and on heating gently with a small flame a certain amount of decomposition took place without explosion. On heating more strongly, however, a violent explosion suddenly occurred, and at the same time a further quantity of the nitride, which was contained in another portion of the apparatus, also exploded.

A further small sample was dissolved in dilute acid, and an ammonium salt was found to be produced in the normal manner.

Mercury Nitride (Hg_3N_2).

Plantamour in 1841[†] passed gaseous ammonia over yellow mercuric oxide, first in the cold and later at a temperature of 130° C., an explosive dark brown powder being obtained. This was analysed by Hirzel,[*] who stated that it corresponded to the formula Hg_3N_2. Later investigators have found that the product always contains oxygen,[†] but it would not appear to be definitely proved whether this is, as would be expected, present in the form of unchanged mercuric oxide, or whether a definite compound is formed, for the composition of which the formula $Hg_2 : NOH$ has been suggested. Hoffmann and Marburg[‡] ascribe this formula also to the product obtained by heating Millon's base in ammonia. The body prepared in either of these ways consists of a dark brown powder, which explodes easily by friction or heat or on solution in concentrated sulphuric acid.

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[*] Ann. der Physik. (4), 1900, 1, 700.

[†] Annalen, 1841, 40, 115.

It reacts normally with dilute hydrochloric acid, with production of ammonia and of mercuric chloride. On being heated with powdered caustic potash ammonia is evolved without explosion, provided that the substances are well mixed.

Mercuric nitride has been prepared in a state of purity by Franklin,[§] who allowed mercuric iodide to react with potassamide in liquid ammonia solution:

$$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$$

A chocolate-coloured precipitate of nitride is formed, which, after standing for some time, becomes darker and more easily washed with liquid ammonia. It is insoluble in liquid ammonia itself, but dissolves in a solution of potassamide in this solvent. It is highly explosive and must be handled with great care. Franklin states that the nitride explodes when brought in contact with water, but it is probable that this is due to the presence of a trace of potassamide. It was analysed by solution in dilute hydrochloric acid, the mercury being estimated as sulphide and the ammonia by distillation. The composition agreed with the normal formula Hg_3N_2.

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[*] Annalen, 1852, 84, 258.

[†] Weyl. Pogg. Ann., 121, 601; 131, 524.

[‡] Annalen, 1899, 305, 204.

[§] J. Amer. Chem. Soc. 1905, 27, 820.

Fischer and Schröter have also prepared mercury nitride thermally.

Boron Nitride (*BN*).

Boron unites readily with nitrogen when heated to a high temperature in the gas or even in a limited supply of air. Wöhler and St. Claire Deville* found that on heating amorphous boron in a muffle to a moderate temperature, the boron takes fire and burns completely. The product did not, however, consist of boric acid, but of a mixture of this body with boron nitride, and on heating with soda-lime, ammonia was evolved. Similarly a considerable yield of the nitride, also mixed with oxide, may be obtained by heating amorphous boron to redness in nitrous or nitric oxide.

Wöhler† also prepared boron nitride by heating to redness 1 part of dehydrated borax with 2 parts of ammonium chloride, the operation being preferably carried out in a platinum crucible. In view of the volatilisation of the ammonium chloride the yield of nitride is low, and Moeser and Eidmann‡ recommend heating a mixture of borax with a porous inert material, such as tricalcium phosphate, in the vapour of ammonium chloride in a combustion tube. Before treatment with ammonium chloride the mixture of phosphate and borax is preferably subjected to a preliminary heating in a crucible, and the porous mass thus obtained is used for the preparation.

At the temperature of the combustion furnace about 50 per cent. of the theoretical yield of boron nitride is obtained, but at a lower temperature only the first of the following reactions takes place:

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* Compt. Rend., 1858, 46, 185.

† Annalen, 1850, 74, 71.

‡ Ber., 1902, 35, 535.

(*a*) $2NH_4Cl + Na_2B_4O_7 = 2NaCl + 2NH_3 + 2B_2O_3 + H_2O$.

(*b*) $B_2O_3 + 2NH_3 = 2BN + 3H_2O$

In order to prepare larger quantities by the same method Moeser and Eidmann recommend the use of a large crucible, through the lid of which a porcelain tube is inserted. The crucible is charged with the calcined mixture as before, and is then heated in a furnace to 1200°–1400° C., a current of ammonia being led in through the porcelain tube. The product is washed free from tricalcium phosphate by means of water containing a small proportion of hydrochloric acid. The nitride usually contains boric acid, which is difficult to remove. Its nitrogen content was found to vary between 47·6 and 53·8, the formula BN requiring about 56 per cent. of nitrogen.

It is also possible to prepare boron nitride according to the second of the above equations, by leading ammonia over boron trioxide at a temperature of about 800°, a yield of 65 per cent. of that theoretically possible being reported under these conditions. Other methods of preparation consist in passing the vapour of boron trichloride together with excess of ammonia through a hot tube, or heating boron trioxide with potassium or mercury cyanide.

Stock and Blix* prepared boron nitride in a state of purity by heating borimide to a temperature exceeding 130°, when ammonia is given off and the nitride remains.

$$B(NH)_3 = 2BN + NH_3$$

Boron nitride is a white amorphous mass, which is not attacked either by ordinary acids or by aqueous alkalies. It is, however, acted upon by hydrofluoric acid, with production of ammonium borofluoride. It is also unchanged on being heated in hydrogen or in chlorine. The nitride may be hydrolysed in the normal manner by heating in a current of steam, or by fusion with potassium hydroxide:

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* Ber., 1901, 34, 3044.

$$BN + 3H_2O = NH_3 + H_3BO_3$$

It is not easily oxidised, but burns when introduced into the flame of a blowpipe.

When heated with reducible metallic oxides, boron nitride reduces these with production of oxides of nitrogen; thus, with mercuric oxide, lead oxide or copper oxide red fumes are formed. It reacts, further, with anhydrous potassium carbonate, a mixture of potassium borate and cyanate being obtained after fusion. When prepared by Stock's method (by heating borimide), boron nitride is more reactive than when prepared at a high temperature in that it is attacked by aqueous caustic soda, but the preparation loses this additional reactivity on being heated.

Aluminium Nitride (*AlN*).

Brieglieb and Geuther in 1862* obtained aluminium nitride by heating aluminium turnings in a hard glass combustion tube in an atmosphere of nitrogen. An increase in weight was noted, and the product, when fused with potash, was found to evolve ammonia. White and Kirschbraun† state that aluminium nitride may also be formed by the action of ammonia on aluminium at 700°, but the reaction is incomplete.

Aluminium nitride is manufactured commercially as a method of nitrogen fixation. According to Serpek's‡ procedure, finely divided alumina is subjected to preliminary heating in an inclined tube A (see Fig. 13), of a type similar to that employed for the manufacture of cement. It is then mixed with powdered coke and fed into a second inclined tube B, which contains an electrically heated section C. In this part of the plant the temperature of the charge is raised to 1800° C.

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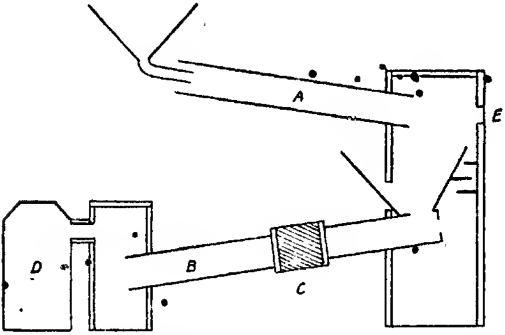
* Annalen, 1862, **123**, 238.
† J. Am. Chem. Soc., 1906, **28**, 1343.
‡ Brit. Pat., 13086/10.

Reaction takes place according to the equation :

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$$

The nitrogen required is derived from producer gas, generated in D, this gas passing through the

FIG. 13.



system in countercurrent to the solid materials employed, and being used, after injection of secondary air at E, for the preliminary heating of the aluminium oxide in A.

Nitrides of the Rare Earths.

Matignon* has obtained nitrides of various rare earths by reducing an oxide of the element in question by means of magnesium or aluminium in a nitrogen atmosphere. As a variation of the method sodium was used to reduce a chloride in nitrogen.

The preparation was carried out in a simple manner by mixing several grams of the oxide with a slight excess of magnesium powder, the mixture being placed in a hard glass tube connected with a supply of nitrogen and with a manometer. After filling the tube with nitrogen, connection with the gas supply was shut off by means of a stopcock and the tube was heated in a combustion furnace. Reaction with incandescence and immediate production of a vacuum was found to occur with lanthanum oxide (La_2O_3), praseodymium oxide (Pr_2O_3), neodymium oxide (Nd_2O_3), and samarium oxide (Sa_2O_3).

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* C.R., 1900, 131, 837.

Lanthanum nitride was examined in detail by Muthmann and Kraft.* It is formed by heating the metal to 850°–900° C. in pure nitrogen. Absorption took place gradually, and without the vivid incandescence reported by Matignon. The product contained slightly over 9 per cent. of nitrogen, corresponding to the formula LaN, which requires 9·15 per cent. of nitrogen.

Lanthanum nitride is black, and is changed by moist air with formation of ammonia. It reacts with water less violently than cerium nitride, and according to the equation—

$$LaN + 3H_2O = La(OH)_3 + NH_3$$

It dissolves in acids in the normal manner.

In place of nitrogen, ammonia may also be used for its preparation.

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* Annalen, 1902 325, 274.

CHAPTER V.

NITRIDES OF GROUPS IV, V AND VI OF THE PERIODIC SYSTEM.

Carbon Nitride, Cyanogen (C_2N_2).

CYANOGEN is apparently not formed by the direct union of carbon and nitrogen.

It is most readily prepared by heating mercuric cyanide.

$$Hg(CN)_2 = Hg + C_2N_2$$

An alternative and more convenient method of obtaining cyanogen consists in allowing a concentrated solution of an alkaline cyanide to react with a solution of a cupric salt.* Cupric cyanide, which is probably the first product formed, is unstable, being immediately resolved into cuprous cyanide and cyanogen:

$$2CuSO_4 + 4KCN = 2CuCN + C_2N_2 + 2K_2SO_4$$

It is a colourless gas with a characteristic odour, and condenses to a colourless liquid at −34·4° C.

Cyanogen is also capable of existing in a polymeric form known as paracyanogen. This is a brown solid, which is formed as a residue on heating mercuric cyanide for the preparation of cyanogen. On being heated, it slowly passes into the ordinary gaseous modification.

A further binary compound of carbon and nitrogen has been prepared by Moreu and Bougrand† by

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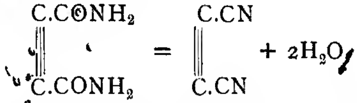
Jacquemin Ann. Chim. Phys., 1886 (6), 6, 140.
C.R., 1910 150, 225.

dehydrating butine diamide, the corresponding dinitrile being obtained:



$$\begin{array}{c} \text{C.CONH}_2 \\ ||| \\ \text{C.CONH}_2 \end{array} = \begin{array}{c} \text{C.CN} \\ ||| \\ \text{C.CN} \end{array} + 2H_2O.$$

Its vapour density corresponds to the formula given. The compound is, however, generically different from the nitrides generally, and only merits its proposed name of "carbon subnitride" by reason of its binary composition.

Silicon Nitride (Si_2N_3).

Deville and Wöhler* in 1859 found that on heating crystalline silicon in a crucible, which was protected from atmospheric oxygen by means of a larger crucible containing carbon, the silicon combined with nitrogen, forming a product which, when fused with potash, evolved ammonia. Schützenberger,† repeated Deville and Wöhler's work, employing a wind furnace as a source of heat. After cooling, the silicon was found to be transformed for the greater part into a white substance which could easily be detached and powdered. The space between the crucibles was also filled with a voluminous greenish or bluish-white powder, and each of these preparations was found to evolve ammonia on fusing with potash as above. The combination of silicon with nitrogen is stated by Geuther‡ to take place only slowly at temperatures below its melting-point, it being found that on heating calcium silicide or magnesium silicide to a bright red heat in nitrogen, the calcium or magnesium only combines, leaving the silicon unattacked.

In order to prepare the body in a state of purity for the purpose of determining its composition, Schützenberger* heated crystalline silicon in a porcelain boat to a white heat in a current of nitrogen, a white reaction product being obtained. This was purified from free silicon by being washed with hot aqueous potash, and was analysed by heating with potassium chromate and litharge, the nitrogen evolved being collected and measured. The composition of the preparation was found to correspond to Si_2N_3.

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* Annalen, 1859, 110, 248.
† C.R., 1879, 89, 644.
‡ J. pr. Chem., 1865, 95, 425.

Silicon nitride is not easily attacked by aqueous alkalies, but on fusion with solid potash or soda, ammonia is, as already stated, evolved. It is also easily decomposed by treatment with steam, amorphous silica being produced. A form of silicon nitride, which appears to be more easily attacked by aqueous alkalies, is obtained by the action of ammonia on silicon tetrachloride. Weiss and Engelhardt† state that three distinct nitrides, SiN, Si_2N_3 and Si_3N_4, are formed by the action of nitrogen on silicon.

Nitrides of Titanium.

Titanium unites readily with nitrogen at high temperatures with formation of titanium nitride; indeed, Wöhler and St. Claire Deville‡ point out that the affinity between the two elements is sufficiently great to render difficult the preparation of titanium by reduction, owing to the penetration of atmospheric nitrogen. For this reason, titanium prepared by Berzelius' method, by placing a mixture of potassium titanofluoride and metallic sodium in a crucible, brasqued by a larger crucible containing carbon, contains a considerable proportion of reddish-brown nitride. For the preparation of titanium nitride by this method an extremely high temperature is not necessary, it being found sufficient to place the mixture of potassium titanofluoride and sodium in a porcelain boat contained in a hard glass, or preferably porcelain, tube, which is heated in a combustion furnace in a current of nitrogen. The salt is transformed into a bronze-coloured mass, which is not appreciably soluble in boiling concentrated hydrochloric acid, but which, when fused with potash, evolves ammonia. The nitride may also be obtained by leading the vapour of titanium chloride, carried by a current of hydrogen and nitrogen, over metallic sodium.

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* C.R., 1881, 92, 1508.

† Z. f. anorg. Chem., 1909, 65, 38.

‡ C.R., 1857, 45, 480.

In place of synthesising the nitride by the action of free nitrogen on the metal, the compound of titanium chloride with ammonia, $TiCl_4.4NH_3$, may be heated in a current of ammonia, when the same nitride, which, according to Wöhler, possesses the composition Ti_3N_4,[*] is produced.

A dark blue nitride of titanium, TiN_2, was obtained by Wöhler by strongly heating titanium dioxide in ammonia.

Moissan[†] prepared titanium nitride by heating a mixture of titanium oxide and carbon in an electric furnace in the presence of air or nitrogen. Prepared in this way titanium nitride is a yellow-bronze coloured mass, which has been fused during production. Its density is 5·18, and Moissan's product was found to be sufficiently hard to scratch ruby. The percentage of titanium varied from 78·3 to 78·7, corresponding to the formula TiN.

Zirconium Nitrides (Zr_2N_3 *and* Zr_2N_8).

Of these nitrides, Zr_2N_3 appears to be the more clearly defined. It was obtained by Matthews[‡] together with a second nitride, to which the formula

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[*] Wöhler, Annalen, 1850, 73, 34.

[†] C.R., 1895, 120, 290.

[‡] J. Amer. Chem. Soc., 1898, 20, 843.

Zr_2N_2 is ascribed by heating zirconium chloride with ammonia.

Zr_2N_3 has also been prepared by Wedekind* as a by-product during the reduction of zirconia by magnesium in an open crucible.

The nitride is a greenish-brown crystalline powder, which takes fire on being heated gently in contact with air. It is insoluble in acids, with the exception of hydrofluoric, but dissolves slowly in boiling aqueous caustic soda. It is easily decomposed when fused with molten caustic alkalies, with evolution of ammonia. Zirconium nitride is attacked by chlorine or bromine at a red heat with formation of zirconium chloride. It is most readily analysed by oxidising in an atmosphere of carbon dioxide, the nitrogen evolved being collected and measured. A sample treated in this manner was found by Wedekind to contain 81·3 per cent. of nitrogen, the formula Zr_2N_3 requiring 81·2 per cent.

Cerium Nitride (CeN).

This body may readily be obtained by the method adopted by Matignon for the preparation of nitrides of the rare earths (*q.v.*). The reaction is, however, comparatively slow.

Muthmann and Kraft† examined the absorption of nitrogen by cerium in greater detail. The reaction takes place slowly at a moderate red heat, but on raising the temperature to about 850° C. sudden and violent reaction was observed, this being accompanied by incandescence of an intensity comparable with an arc-light. The increase in weight obtained after combination corresponded on an average to a nitride containing 8·2 per cent. of nitrogen. The formula CeN requires 9·1 per cent. On checking the composition by dissolving in dilute sulphuric acid and estimating the ammonia formed, it was found that the results obtained differed from those calculated from the increase in weight, in that the nitrogen content appeared to be about ½ per cent. too low. This was explained by the violence with which cerium nitride is decomposed by diluted acids, a small proportion of the nitrogen escaping in an elementary condition.

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* Z. f. anorg. Chem., 1905, 45, 18.

† Annalen, 1902, 325, 268.

Provided that pure nitrogen is employed for its preparation, the nitride obtained is a bronze-coloured mass, which is often black on its surface. If nitrogen containing small quantities of oxygen or oxides of nitrogen is taken, the product is dark grey and contains oxide.

Cerium nitride is unchanged in dry air, but in contact with moisture ammonia is evolved; the mass becomes hot and finally glows, being oxidised to cerium dioxide. Its heat of reaction with water is sufficient to raise the dioxide produced to a bright-red heat if a few drops only of the water are sprinkled on to a small quantity of the nitride. At the same time hydrogen and ammonia are evolved according to the equation

$$2CeN + 4H_2O = 2CeO_2 + 2NH_3 + H_2$$

and burn spontaneously, the residue consisting of pure cerium dioxide.

On the other hand, solution in aqueous potash takes place with only moderate velocity, ammonia and cerous hydroxide being formed.

It dissolves in dilute mineral acids, forming cerous salts and ammonium salts:

$$2CeN + 4H_2SO_4 = Ce_2(SO_4)_3 + (NH_4)_2SO_4$$

This reaction often takes place with incandescence, and, by reason of its high temperature, leads to the loss of nitrogen noted in the analysis quoted above.

Thorium Nitride (Th_3N_4).

Thorium nitride is formed by heating thorium to a red heat in nitrogen,[*] or by Matignon's method given for the rare earths.

Moissan[†] obtained thorium nitride by the action of ammonia on thorium carbide.

The nitride decomposes water slowly in the cold and rapidly at 100°C. With dilute acids and with aqueous alkalies it reacts normally, forming ammonia. Thorium nitride burns when heated in oxygen, without, however, the vivid incandescence produced by thorium itself.

It may be noted that the nitride of thorium prepared by Kohlschütter[‡] by heating a mixture of thoria and magnesium to a high temperature in the presence of nitrogen (*cf.* Matignon), appears to be less reactive than the preparation described above, since it is stated not to be attacked by water, or with dilute acids or alkalies. On fusing with potash ammonia was, however, evolved.

Matignon analysed the compound by measuring the ammonia evolved during solution in aqueous potash, or, alternatively, by noting the increase in weight obtained by heating thorium in nitrogen. In each case the result indicated a formula corresponding to Th_3N_4, this being also possessed by Kohlschütter's preparation.

Tin Nitride.

An impure product containing this body has been obtained thermally by Fischer, Iliovici and Schröter. The product contained about 5 per cent. of nitrogen.

Lead Nitride.

This was prepared as a black powder by Fischer and Schröter by the thermal method already described. It was found to be highly explosive, and was not obtained in a pure condition.

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[*] Matignon, C.R., 1900, 131, 837; 1901, 132, 36.
[†] Le Four Electrique, p. 320.
[‡] Annalen, 1901, 317, 170.

Vanadium Nitrides (VN *and* VN_2).

Vanadium mononitride was prepared by Roscoe[*] by passing ammonia over vanadyl trichloride, contained in a bulb tube, and heating the resulting compound until all ammonium chloride had been volatilised. The remaining black powder was placed in a platinum boat and reheated for several hours to whiteness in a current of ammonia. The nitride obtained in this way consists of a greyish-brown powder, which is unchanged in the air at room temperature, but, on being heated, passes first into the blue oxide of vanadium and at a higher temperature into vanadium pentoxide. On being heated with soda-lime, ammonia is evolved.

Vanadium dinitride was obtained in 1858 by Uhrlaub,[†] who allowed ammonia to act on vanadyl chloride, and heated the product, as in the preparation of the mononitride, until all ammonium chloride had been volatilised. For the preparation of this higher nitride further heating to a white heat is omitted, the product being washed with aqueous ammonia and dried in a vacuum. It is a black powder, which on being heated loses nitrogen and passes into vanadium mononitride. Owing to the use of an incorrect atomic weight for vanadium Uhrlaub did not recognise its true formula, this being pointed out by Roscoe (*loc. cit.*).

Muthmann and Riedelbauch[‡] state that finely divided vanadium reacts directly with nitrogen at a red heat. The reaction is, however, very slow, and it was found necessary to heat 0·1 grm. of the metal from twenty to twenty-five hours at full redness before the increase in weight became constant. The absorption of nitrogen takes place also at a dull red heat, but the action is still slower.

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[*] Annalen, 1868, 6, 77 (Suppl.).
[†] Pogg. Ann., 1858, 103, 134.
[‡] Annalen, 1907, 355, 92.

The nitride thus obtained is a velvety-black powder which is unchanged in air. Water and aqueous hydrochloric acid are without action even on boiling, but it dissolves in cold nitric acid. It is not affected by aqueous alkalies, but when fused with potash, ammonia is given off. On being heated in the air it is converted into vanadium pentoxide. The composition of the product, in contradistinction to the nitrides obtained by Roscoe, appeared to approximate to the formula V_2N.

Niobium Nitride (Nb_3N_5).

Moissan[*] found that on heating niobium powder to 1200° in nitrogen, the metal became covered with a layer of yellow nitride.

Muthmann and Riedelbauch (*loc. cit.*) obtained a product which was black in colour and possessed a composition approximating to Nb_3N_5, similar to that prepared by Roscoe by heating the product obtained by the action of dry ammonia on niobium oxychloride. Niobium nitride was prepared by St. Claire Deville by heating niobic acid to a high temperature in a current of ammonia. The product corresponded to NbN. It may also be obtained in an analogous manner to vanadium nitride by heating the yellow compound of niobium oxychloride and ammonia. It is possible that two nitrides of niobium exist, having the composition NbN and Nb_3N_5 respectively. The properties of niobium nitride resemble those of vanadium nitride except that it is not dissolved by nitric acid.

Nitrides of Tantalum (*TaN and* Ta_3N_5).

As was the case with vanadium and niobium, tantalum chloride reacts in the cold with ammonia, and on gently heating the product to a temperature sufficient to volatilise the ammonium chloride also formed, a yellowish-red nitride of tantalum possessing the composition Ta_3N_5 is obtained. On heating this to whiteness in a current of ammonia, it loses nitrogen and passes into a black nitride, TaN.* Muthmann and Riedelbauch (*loc. cit.*) observed a direct but slow formation of tantalum nitride by heating the finely divided metal to 1200° in nitrogen.

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[*] C.R., 1901, 133, 20.

Tantalum nitride is not attacked by aqueous acids or alkalies, but evolves ammonia on fusion with the latter reagents.

Phosphorus Nitride (P_3N_5).

Stock and Hoffmann† have prepared a nitride of phosphorus, possessing the composition given, by heating an additive compound of phosphorus pentasulphide and ammonia to 230° C.

It is a colourless and tasteless body which is insoluble in water, and is decomposed at a red heat into its elements. On being heated in hydrogen ammonia is formed, and on being boiled with water a slow but normal decomposition into phosphoric acid and ammonia is obtained. The same reaction takes place rapidly and quantitatively at 180° C.

Arsenic Nitride (*AsN*).

Arsenic nitride was obtained by Hugot‡ by heating arsenamide to 250°. The amide was prepared by saturating arsenic chloride, bromide or iodide with ammonia at −30° to −40°, and on being heated was found to pass successively into arsenimide (at 60°) and to the nitride as stated:

$$2As(NH_2)_3 = As_2(NH)_3 + 3NH_3$$
$$As_2(NH)_3 = 2AsN + NH_3$$

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* Rose, Pogg. Ann., 1857, **100**, 146 and 418.

† Ber., 1903, **36**, 314.

‡ C.R., 1904, **139**, 54.

Arsenic nitride is an orange-red body, which is resolved into its elements suddenly and completely at a temperature slightly in excess of that at which it is formed. Arsenic nitride was also formed thermally by Fischer and Schröter.

Antimony Nitride (*SbN*).

Antimony nitride is one of the few nitrides which were prepared by Fischer and Schröter* in a suitable form for analysis. The product was a black powder which exploded on being heated gently, with formation of an antimony mirror. By treating the impure nitride with dilute hydrochloric acid, a separation from admixed free antimony could be effected, the latter remaining undissolved, while the nitride reacted normally, according to the equation—

$$SbN + 4HCl = SbCl_3 + NH_4Cl$$

Bismuth Nitride (*BiN*).

This was obtained by Fischer and Schröter, also by Fischer and Iliovici, in a manner similar to antimony nitride.

Franklin† prepared bismuth nitride by the action of bismuth tribromide or iodide on potassamide in liquid ammonia solution. Presumably bismuth amide is formed as an intermediate compound:

$$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3$$

The nitride is a dark brown precipitate which becomes almost black on drying. It explodes on being heated or on coming in contact with water or with dilute acids. In order to determine its composition it was slowly decomposed by water vapour, the product being dissolved in dilute hydrochloric acid. The composition corresponded to BiN. Fischer and Schröter state that explosion occurs on gently shaking the vessel containing the nitride, this vessel becoming covered by a mirror of bismuth.

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* *Vide* Schröter, Dissertation, Berlin, 1909, p. 68.

† J. Am. Chem. Soc., 1905, 27, 220.

Chromium Nitride (*CrN*).

Schrötter,[*] in the course of his work on nitride formation, passed gaseous ammonia over heated chromium chloride, an impure nitride being obtained. Some twenty years later Brieglieb and Geuther[†] heated metallic chromium to redness in nitrogen in a glass combustion tube. After two hours' treatment an increase of weight, amounting to 13·3 per cent. of the chromium taken, was observed, and on continuing the treatment, after mixing the product in a mortar, preparations were obtained containing 78·9 per cent. of chromium, the remainder being nitrogen.

Brieglieb and Geuther's chromium was prepared by reducing violet chromium chloride by means of zinc. The work was confirmed and extended by Ferée,[‡] who showed that pyrophoric chromium, obtained by decomposing its amalgam at a temperature below 350°, becomes incandescent when heated in a current of nitrogen. The products contained from 78·95 to 79·05 per cent. of chromium. The formula CrN corresponds to 78·9.

The nitride may also be formed by the action of ammonia on pyrophoric chromium or mixed with green Cr_2O_3, by heating the finely-divided metal in nitric oxide.

Chromium nitride is insoluble in hydrochloric acid, nitric acid or aqua regia. On being heated with soda-lime, ammonia is given off.

Molybdenum Nitride.

By the passage of ammonia at an elevated temperature over chlorides or oxides of molybdenum, compounds containing nitrogen are readily obtained, but the pure nitride does not appear to have been isolated.

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[*] Annalen, 1841, 37, 148.

[†] Annalen, 1862, 123, 239.

[‡] Bull. Soc. Chim., 1901, 25, 618.

The use of a high pressure has also been suggested, the oxide being heated to 500°–600° C. in a mixture of nitrogen and hydrogen at a pressure of 50 atmospheres.

Tungsten Nitride (W_2N_3).

Metallic tungsten does not react directly with nitrogen or with ammonia. A nitride, W_2N_3, was obtained by Wöhler* by the action of ammonia on tungsten oxytetrachloride or hexachloride.

It is a black powder, which is insoluble in aqueous alkalies and in dilute sulphuric acid, but is converted by concentrated sulphuric acid into ammonium sulphate and tungstic acid.

Uranium Nitride (U_3N_4).

Moissan† states that uranium unites directly with nitrogen at 1000° C., or with ammonia at a lower temperature, a yellow nitride being formed. This may also be prepared by heating uranium carbide in nitrogen to 1100° in an electric furnace, but the reaction is incomplete.

An impure nitride of uranium was obtained in 1861 by Uhrlaub‡ by heating uranium tetrachloride in ammonia, the product being finally heated in the vapour of ammonium chloride.

Kohlschütter§ repeated the above work. Uranium chloride was prepared by heating uranium carbide in a current of chlorine in a hard glass bulb-tube. Dry ammonia was next passed over the product, the heating being continued, when the dark green crystalline body melted to a black liquid, which, as the reaction proceeded, became solid once more. A definite compound was not obtained. The product contained chlorine, and became oxidised when it was ground in a mortar for re-treatment. As a convenient method of preparing the nitride, Kohlschütter recommends the reduction of uranium oxide by means of aluminium or magnesium in a nitrogen atmosphere. Aluminium nitride is only formed to a very slight extent, the main reaction being represented by the equation:

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* Annalen, 1850, 73, 190; 1858, 105, 258; Rideal, J. Chem. Soc., 1889, 55, 41.

† C.R., 1896, 122, 274.

‡ Dissertation, Göttingen, 1861, Verbindung einiger Metalle mit Stickstoff.

§ Annalen, 1901, 317, 165.

$$16Al + 3U_3O_8 + 6N_2 = 3U_3N_4 + 8Al_2O_3$$

A similar preparation with magnesium as the reducing agent presents the advantage that the by-products are more easily soluble. In an experiment 848 parts of U_3O_8 and 192 parts of dry and finely-divided magnesium were mixed in a warm and dry mortar, about 4 grm. of this mixture being placed in a porcelain boat and heated to redness as in nitrogen. The reaction, when once started, went quickly. When absorption of nitrogen had stopped, the product was washed first with water, afterwards with dilute hydrochloric acid, magnesium nitride or oxide being thus removed.

Uranium nitride is a stable body, being unattacked by concentrated hydrochloric or sulphuric acid. Oxidising acids, however, quickly decompose it.

Kohlschütter states that his product was unchanged by aqueous alkalies, while on fusion ammonia was evolved normally. The nitride prepared from carbide by Moissan's method was, however, decomposed by boiling with aqueous potassium hydroxide.

When heated in air, uranium nitride burns to pure U_3O_8. It may easily be analysed by the combustion method, using copper oxide and lead chromate.

Nitrogen Sulphides.

Nitrogen sulphide (N_4S_4) is prepared by passing dry ammonia into a solution of sulphur dichloride in benzene.* It crystallises from carbon disulphide solution in orange needles, which melt at 178° and are highly explosive. For this reason the body is preferably stored in cardboard boxes and not in glass bottles.*

In properties it resembles the true nitrides by reacting with water to form ammonia. It dissolves in benzene or carbon disulphide and unites directly with the halogens, forming additive compounds; thus with bromine, among other compounds, $N_4S_4Br_4$ is obtained as bronze crystals from carbon disulphide solution.† When heated gently in the same solvent, a further sulphide of nitrogen, having a formula corresponding to N_2S_5, is found among the decomposition products. This is a red liquid at ordinary temperatures, solidifying at 10° C.‡

Nitrogen Selenide (Se_2N).

Nitrogen selenide was discovered by Wöhler in 1859, the method of preparation consisting in leading gaseous ammonia into selenium tetrachloride. It was obtained in a pure condition by Verneuil,§ by carrying out the above reaction in carbon disulphide solution. Selenium nitride is an orange powder which is highly explosive and possesses the composition given.

Nitrogen Telluride (TeN).

This compound was obtained by Metzner‖ in an analogous manner to the selenide, by allowing tellurium tetrachloride to act on liquid ammonia at low temperatures. The product was freed from ammonium chloride by being washed with ammonia, and finally with water. It is a lemon-yellow powder, which explodes on being heated to 200° C., or on being subjected to a shock.

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* Schenk, Annalen, 1896, **290**, 171.

† Clever and Muthmann, Ber., **29**, 340.

‡ Clever and Muthmann, Z. f. anorg. Chem., 1896, **13**, 200.

§ Bull. Soc. Chim. (2), 1882, **38**, 548.

‖ C.R., 1897, **124**, 32.

The nitride is not attacked by water or by dilute acetic acid, but on being heated with potash evolves ammonia.

CHAPTER VI.

NITRIDES OF GROUPS VII AND VIII OF THE PERIODIC SYSTEM.

Manganese Nitride.

THIS body was obtained by Prelinger[1] by heating manganese amalgam to a red heat in a current of nitrogen. If the heating is carried out quickly, the reaction is sufficiently vigorous to cause the mass to glow even in daylight. The nitride consists of a slate-grey powder, which evolves ammonia on being heated in hydrogen or with molten alkalies. It was analysed by solution in dilute hydrochloric acid, the ammonia formed being estimated by distillation. The products contained from 9–9·5 per cent. of nitrogen.

On substituting ammonia for nitrogen in the above preparation, a nitride containing about 13·6 per cent. of nitrogen was formed. Prelinger considered that this body is distinct from that obtained by the direct union of the elements, and assigns to the two nitrides the formulæ Mn_5N_2 and Mn_3N_2, corresponding to 9·2 and 14·5 per cent. of nitrogen respectively. The latter body is stated to be less easily attacked by steam, dilute sulphuric acid or aqua regia than Mn_5N_5, and to be somewhat darker and more metallic in appearance.

Manganese nitride is also formed in small proportions by heating manganese in a limited volume of air.

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[1] Monatsh., 1894. 15, 391.

Nitrides of Halogens.

These bodies, which may be regarded as halogenated ammonias, have, since the time of their discovery, now over a hundred years ago, attracted considerable interest on account of their highly explosive properties.

Nitrogen chloride is formed in various ways by the interaction of chlorine or of hypochlorous acid with ammonia or ammonium chloride. Gattermann has shown that the reaction product obtained by the action of chlorine on aqueous ammonium chloride usually contains, in addition to incompletely chlorinated derivatives of ammonia, a considerable proportion of free chlorine, which is dissolved by the nitrogen chloride. In order to prepare the pure trichloride, this reaction product is washed with water—an operation which requires considerable care—and exposed once more, in a thin layer, to the action of chlorine.*

It is also easily prepared by allowing a solution of ammonium chloride to react with an excess of dilute hypochlorous acid, the resulting mixture being extracted with benzene. Calcium hypochlorite is not suitable for this preparation unless special conditions of concentration are observed.† In place of benzene, nitrogen chloride may, particularly with a view to studying its properties, be dissolved in carbon disulphide, chloroform, ether, carbon tetrachloride and other solvents. Dilute solutions of this nature are far less dangerous than the pure substance, it being stated by Hentschel‡ that a 10 per cent. solution of nitrogen chloride in benzene may even be ignited without exploding.

Noyes and Lyon§ have shown that the normal reaction for the formation of nitrogen chloride from chlorine and ammonia

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* Gattermann, Ber., 1888, **21**, 751.

† Hentschel, Ber., 1897, **30**, 2642.

‡ Ber., 1897, **30**, 1434.

§ J. Am. Chem. Soc., 1901, **23**, 460.

$$12NH_3 + 6Cl_2 = N_2 + NCl_3 + 9NH_4Cl$$

only takes place when ammonia and chlorine are employed in the stoichiometric proportions required.

If an excess of ammonia is used, this reacts with a portion of the nitrogen chloride, giving free nitrogen and also probably ammonium hypochlorite,*

$$NCl_3 + 4NH_3 = N_2 + 3NH_4Cl$$
$$NCl_3 + 2NH_4OH + H_2O = 3NH_4ClO.$$

The effect of an excess of chlorine, on the other hand, would appear to be merely that this reacts with the ammonium chloride formed by the reaction, with formation of a further quantity of nitrogen chloride.

Nitrogen chloride is a yellow liquid which explodes in sunlight or on heating, also often spontaneously. Explosion may also be induced by contact with turpentine or phosphorus.

Nitrogen bromide is most readily prepared by the double decomposition of nitrogen chloride with aqueous potassium bromide. It does not appear to have been studied as extensively as the chloride, but is equally explosive.

Nitrogen iodide, as usually prepared by the action of iodine on aqueous ammonia, consists rather of the compound $NI_3.NH_3$ than of the pure iodide.†

A similar compound, but containing three molecules of associated ammonia, has been obtained by Hugot‡ by passing dry gaseous ammonia into a cooled vessel containing iodine. The colour of the liquid changes from dark brown to red, and finally to yellow, a compound having the composition $NI_3.3NH_3$ being precipitated from the liquid ammonia solution in dark-green needles. The reaction takes place according to the equation:

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* Schönbein, J. prakt. Chem., 1861, 84, 386; Fresenius, Zeitschr. f. anal. Chem., 1863, 2, 59.

† Chattaway and Orton, Am. Chem. J., 1900, 23, 363; 24, 342.

‡ C.R., 1900, 130, 505.

$$4NH_3 + 6I = NI_3.3NH_3 + 3HI.$$

On allowing the compound $NI_3.3NH_3$ to rise in temperature in a vacuum, it loses one molecule of ammonia at − 30° and a second molecule at 0° C., with formation of $NI_3.2NH_3$ and $NI_3.NH_3$, respectively. It is not found possible to drive off the remaining molecule of ammonia, since a violent detonation occurs on heating to about 50° C.

A further method of preparing nitrogen iodide in a state of purity consists in allowing iodine trichloride to react with well-cooled aqueous ammonia, this method being particularly adapted to the safe preparation of comparatively large quantities of the pure iodide.

Nitrogen iodide, in addition to its explosive properties when dry, undergoes slow decomposition, even when kept in a moist state, nitrogen, hydriodic and hypo-iodous acids and ammonia being formed.

Nitrides of the Transition Elements.

Nitrides have been described of iron, cobalt and nickel, that of iron being by far the best known. No nitrides of the platinum metals have up to the present been obtained.

Iron Nitride.

Despretz in 1829* prepared iron nitride, containing from 7 to 10·5 per cent. of nitrogen, by heating iron in a current of ammonia, this result being confirmed subsequently by Buff† and Rogstadius,‡ who obtained products containing 9 per cent. of nitrogen as a maximum. More recently the formation of iron nitride by the action of ammonia on metallic iron has been studied by

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* Ann. Chim. Phys., 1829, **42**, 122.

† Annalen, 1852, **83**, 375.

‡ J. prakt. Chem., 1862, **86**, 307.

Fowler,* Beilby and Henderson,† White and Kirschbraun‡ and by the author.§ The iron is preferably employed in a finely divided condition, such as is obtained by reduction from the oxide, the most suitable temperature for forming the nitride being about 460° C., but higher temperatures may be employed provided that the current of ammonia is rapid. The use of substantially higher temperatures is, however, accompanied by the formation of a product less rich in nitrogen than that obtained at or about 460° C. In no case is a pure compound obtained, the reaction product consisting of nitride together with a certain proportion of unchanged iron.

In order to obtain a product containing a maximum percentage of combined nitrogen, the ammonia employed should be dry and free from oxygen, and the product may advantageously be well mixed by grinding in a mortar several times in the course of the treatment. A certain amount of the unchanged iron may be removed from the product by magnetic separation, the nitride itself being non-magnetic. In a typical preparation, about 3·5 grm. of precipitated iron oxide were weighed out in a porcelain boat and reduced to metal by means of hydrogen at 700° C. The hydrogen was now replaced by a current of dry oxygen-free ammonia—which is conveniently obtained from liquid ammonia containing sodium in solution in order to eliminate traces of moisture—whereupon the temperature was decreased to 480° for four hours, then to 460° for a further period of six hours. The product, which already contained a high proportion of nitride, was cooled in ammonia, weighed, and subjected to magnetic fractionation, the less magnetic portion being replaced in the boat and heated for a further four hours in ammonia, during which period the temperature was gradually decreased from 460° to 420° C.

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* J. Chem. Soc., 1901, 79, 285.

† J. Chem. Soc., 1901, 79, 1245.

‡ J. Amer. Chem. Soc., 1906, 28, 1343.

§ Dissertation, Berlin, 1911.

Working in this way, it was found possible to obtain products containing about or slightly over 11 per cent. of combined nitrogen, which was estimated by solution in dilute hydrochloric acid and subsequent distillation in the usual way.

The formula Fe_4N_2 corresponds to 11·1 per cent. of nitrogen, but it is not clear whether the compound obtained corresponds with this formula, or whether it consists of a mixture of the normal nitride Fe_3N_2, which would be expected from its mode of formation, with unchanged iron.

Iron nitride may also be obtained by the action of ammonia on an oxide or a suitable salt, such as ferrous chloride. It may be noted that iron nitride of the normal composition Fe_3N_2 has been obtained by Guntz by the action of lithium nitride on a ferrous salt.

Contrary to the statements of Frémy* and Geuther and Brieglieb,† it is not formed by the action of free nitrogen on iron, either at ordinary pressures‡ or by heating iron in nitrogen in a sealed tube.§ A similar negative result has been obtained by the author,‖ even with nitrogen under a pressure of 200 atmospheres.

A further and most interesting method of forming this nitride has been described by Wolk,¶ who states that if a mixture of barium and iron amalgam is heated quickly to 1000° in a nitrogen atmosphere, the barium nitride formed contains also some iron nitride. In view of the fact that iron nitride is normally decomposed at this temperature, confirmation of its formation by this method would appear to be desirable.

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* C.R., 1861, 52, 321.

† Annalen, 1862, 123, 228.

‡ Stahlschmidt, Pogg. Annalen, 1865, 125, 137.

§ Fowler, J. Chem. Soc., 1901, 79, 285.

‖ J. Soc. Chem. Ind., 1918, 37, 108T.

¶ Bull. Soc. Chim. (3), 1902, 27, 153.

Iron nitride is a dull grey powder, which easily dissolves in dilute hydrochloric or sulphuric acid, with formation of ammonium salts and of ferrous salts. When heated in oxygen to about 200° C. it passes into ferric oxide without the production of oxides of nitrogen. In chlorine it readily takes fire, forming ferric chloride, but bromine and iodine are without action on it.

Nitric oxide reacts with iron nitride with production of iron oxide and free nitrogen, while with carbon dioxide a mixture of carbon monoxide and nitrogen is formed, the iron being similarly oxidised.

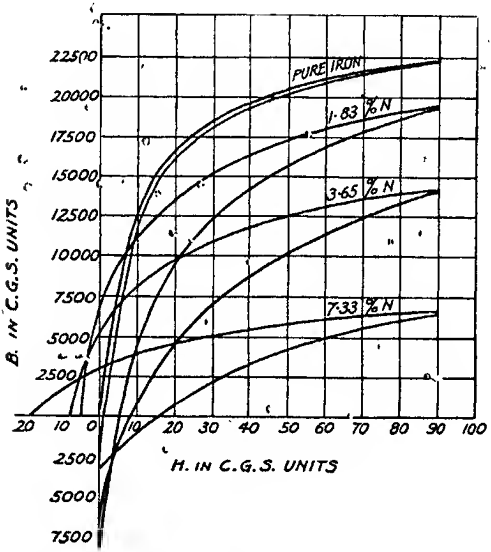
When heated in steam at 100° C. ammonia is slowly evolved. With hydrogen sulphide a somewhat similar reaction takes place, ammonium sulphide and ferrous sulphide being obtained. When heated with carbon no cyanogen is formed, but on adding sodium to the mixture sodium cyanide is produced.

Iron nitride, containing a comparatively high percentage of nitrogen, is only weakly magnetic. The quantitative influence of various percentages of combined nitrogen on the magnetic properties of pure iron has been examined by the author, a typical series of hysteresis curves being reproduced in Fig. 14.

The last traces of combined nitrogen are not easily removed from the nitride by the action of heat, it being found in a typical instance that on heating a specimen which originally contained 3·6 per cent. of this element in a vacuum to 1000° C. one hour, 0·2 per cent. of combined nitrogen still remained. This nitrogen content caused the magnetic properties to differ considerably from pure iron, and a further period of seven hours at 1300° C. was necessary before the nitrogen was completely driven off and the original magnetic properties restored. The heat of formation of iron nitride has been determined by

Fowler and Hartog* by measuring the heat evolved on dissolving a known weight of the nitride in dilute sulphuric acid. The value obtained was 3040 cals. for the formation of 1 grm. molecule of nitride, which for this purpose was taken as having a composition corresponding to Fe_2N.

Fig. 14.



Nickel Nitride.

The formation of nickel nitride is stated by Beilby and Henderson† to take place on heating metallic nickel in a current of ammonia to 500° C. The

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[*] Trans. Chem. Soc., 1901, 79, 299

[†] J. Chem. Soc., 1901, 79, 1251.

maximum amount of nitrogen fixed at this temperature corresponded to a product containing 7·5 per cent. of nitrogen.

Nickel nitride is a dull black powder, which is seen under the microscope to consist of aggregates of minute, roughly spherical particles. It is soluble in dilute hydrochloric or sulphuric acid with formation of ammonium salts. When heated in steam or to redness in hydrogen ammonia is given off, this, in the latter case, being accompanied by free nitrogen.

Vournasos* describes the preparation of nickel nitride, which was found to possess the normal formula Ni_3N_2, by allowing a mixture of anhydrous nickelous oxide and cyanide to fall in small quantities at a time through an arc between carbon poles in a nitrogen atmosphere. The nitride is stated to burn in oxygen, forming nitrogen peroxide.

Cobalt Nitride.

Beilby and Henderson† obtained a nitride of cobalt by a similar method to that used for nickel. The limits of temperature for the formation of cobalt nitride from the metal and ammonia are far narrower than for iron, and in order to obtain a product containing a maximum percentage of combined nitrogen —which in Beilby and Henderson's experiments amounted to 10·33 per cent.—these authors recommend an initial temperature of 470° C., which may subsequently be lowered as the absorption of nitrogen proceeds. The reactions of cobalt nitride with dilute sulphuric or hydrochloric acid, also with steam and hydrogen, are similar to those of nickel nitride.

Cobalt nitride is stated by Vournasos to be formed by heating a mixture of cobalt oxide or cyanide by dropping this through an arc as for nickel nitride. The product was a brown powder possessing the composition Co_3N_2.

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* C.R., 1919, 168, 889

† *Loc. cit.*

CHAPTER VII.

ACTIVE NITROGEN.

IT has long been known[*] that on passing a condensed induction discharge through rarefied nitrogen of ordinary purity a yellow luminescence is observed, and that this luminescence persists for a considerable time—in certain circumstances up to several minutes—after discontinuing the discharge.

The phenomenon was investigated in detail by Strutt,[†] who made the most interesting observation that nitrogen, while in this luminous condition, possesses certain active properties, and by virtue of these is able to enter into various chemical reactions which are not obtained with the ordinary gas. To nitrogen in this state the name of "active nitrogen" was given.

The general arrangement of apparatus employed by Strutt is shown diagrammatically in Fig. 15.

It consists of a discharge tube A connected with an induction coil B, which should have a spark-length of at least 6 in. In order to obtain a condensed discharge, a condenser C, together with a spark-gap D, is included in the system. The nitrogen itsel was, in Strutt's earlier experiments, obtained from large gas-holder in which nitrogen was stored ove water, the gas being freed from oxygen by hanging in the holder a perforated metal bucket containing phosphorus, or directly from a cylinder of commercial nitrogen, with the interposition of a heated copper purification tube. In later work these sources of nitrogen were replaced by a large glass globe of four litres' capacity containing metallic sodium heated to 300° C., this form being shown in the figure.

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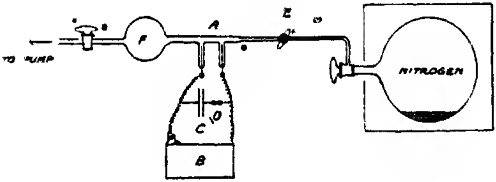
[*] Morren, Ann. chim. et phys., (4) 1865, 293; Sarasin, Pogg Ann., 1876, **140**, 425; Warburg, Arch. de Genève (3), 1884, 1 504; Goldstein, Verhandl. d. deutsch. phys. Ges., 1883, **1**, 16 Lewis, Ann. der Physik (4), 1900, **2**, 459.

[†] Strutt, Proc. R. Soc. (A), 1911, **85**, 219; 1912, **86**, 56, 262 **87**, 179, 302; 1913, **88**, 539; Phys. Ztschr., 1913, **14**, 215.

In any case, the supply of nitrogen is slowly drawn through the apparatus by means of a vacuum pump, as shown, the rate of passage of the gas being regulated by means of the cock E, in such a way that the pressure in the subsequent portions of the apparatus amounted only to a few millimetres of mercury. In order to study the effect of the active gas on various bodies, reaction tubes of suitable character were inserted in place of the observation bulb F shown.

FIG. 15.



On drawing a stream of rarefied nitrogen through the apparatus and starting the discharge, a brilliant orange-yellow luminescence is observed in F. This was of sufficient intensity in some experiments to be visible to an observer 30 ft. away, when the glow was about 18 in. from a 32-candle-power incandescent lamp.

The effect of temperature on the intensity and persistence of this glow has been examined by Strutt, by allowing the glowing gas to traverse a long tube, which could be heated. It was found that the luminescence was extinguished in the heated portion, but reappeared in the cold parts. When cooled by immersing the observation tube in liquid air, the glow of the luminous gas current increased in intensity as the cooled region was approached, but was quickly extinguished on reaching this. In subsequent experiments it was found that the after-glow, under conditions such that this persisted for slightly more than one minute at room temperature, was extinguished in 15 seconds at the temperature of liquid air, the brilliancy being, however, greatly intensified." It is worthy of careful note that the persistence of the after-glow was also decreased at 100°, the brilliancy being, however, diminished at this temperature. A similar intensification of the brilliancy of the glow was obtained by quickly compressing the luminous gas to a pressure of, for instance, 4 cm. above that of the atmosphere.

The chemical properties of active nitrogen are of such a nature that nitrides are formed directly on bringing the glowing gas into contact with many of the elements, which in most cases should be heated gently in order to induce reaction.

As the first example of this phenomenon the case of mercury may be cited. This metal may readily be caused to combine with active nitrogen, either by introducing mercury vapour into a current of the luminous gas, or even, at room temperature, by passage over liquid mercury contained in a U-tube, which is shaken in order to expose fresh surfaces to the action of the nitrogen. The nitride possessed the usual explosive properties, and gave ammonia on being dissolved in acids. Many other metals—for instance zinc and cadmium—become converted superficially into nitride when heated in active nitrogen, while in the cold no reaction is usually obtained. On heating sodium in the gas a series of luminous phenomena is observed. With the sodium at a temperature just above its melting-point, the yellow sodium line is developed with great brilliancy; indeed, the spectroscopic observation of the behaviour of sodium at such low temperatures in nitrogen affords a most delicate qualitative test for the presence of the active modification of this gas. With sodium at 250° a curious effect is obtained. The dense vapour of the metal emits a brilliant green luminescence, and spectroscopic examination shows that the green E line has become greatly intensified, the yellow D line being scarcely visible, but on either side of this green glow an outer luminous portion is obtained, from which the D line of normal relative brilliancy is emitted. In each case absorption of nitrogen takes place.

When drawn over yellow phosphorus, the glow is extinguished and phosphorus nitride formed. The yellow phosphorus is also converted to a certain extent into the red variety. It may be noted that by far the greatest interest in these reactions lies in the fact that they take place after the gas has left the region of discharge. The formation of, for instance, phosphorus nitride in the region of the actual discharge was known prior to Strutt's work—indeed, Strutt states that this effect has been utilised for the exhaustion of incandescent electric lamps.*

Active nitrogen reacts with heated sulphur with the production of a faint blue flame. Nitrogen is absorbed, and a transparent green or blue deposit obtained on the glass wall of the reaction tube. This is the polymeric form of nitrogen sulphide, first prepared by Burt.† It may be noted that on substituting sulphur dichloride for sulphur, the ordinary yellow nitride was formed. With selenium no action was observed.

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* J. Rodet, Lampes à Incandescence, p. 107. Paris: Gauthier Villars, 1907.

† J. Chem. Soc., 1910, 97, 1171.

When passed over iodine at room temperature a remarkable luminous effect is produced. The normal yellow glow is replaced by a brilliant blue flame at the point of confluence of the iodine vapour and nitrogen, this being accompanied by a slight rise of temperature. A green flame is also obtained by heating arsenic in the luminous gas, but the brilliancy of this is low. With thallous chloride, what is described as a magnificent green light is produced, a blue flame being obtained similarly by introducing into active nitrogen the vapour of stannous or stannic chloride.

With nitric oxide a greenish flame, accompanied by a continuous spectrum, is developed at the point of confluence, nitrogen trioxide being formed. This latter may readily be recovered by passage through a U-tube immersed in liquid air. It may be noted, in passing, that an after-glow is also, in certain circumstances, obtained with air in place of nitrogen, and that the luminous effect in this case has been shown by Strutt* to be due to the reaction between nitrogen peroxide and ozone. The spectrum obtained during the reaction between active nitrogen and nitric oxide is identical with the above reaction in air. Active nitrogen does not, on the other hand, combine directly either with oxygen or with hydrogen. Carbon compounds generally, such as acetylene, benzene, methane and other hydrocarbons, also alcohol and ether, react with active nitrogen with the production of the cyanogen spectrum and formation of hydrocyanic acid, the reaction being often accompanied by a lilac flame.

Certain substances, for instance cupric oxide or manganese dioxide, destroy active nitrogen catalytically, without the production of a luminous effect and without increasing in weight. The glow is also extinguished by ammonia and by oxygen in proportions greater than 2 per cent. by volume.

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* Proc. Phys. Soc., 1910, 23, 66.

Active nitrogen conducts electricity to a considerable extent, but Strutt has shown that the number of atoms ionised during the reversion to the ordinary modification is only a small fraction of the whole number concerned in the change, ionisation being a subordinate effect, which may be due to light of very short wave-length emitted during the reaction. The ionisation is found to take place in the glow itself rather than in the discharge. Nitrogen in the active form is a highly endothermic body, but its energy has been shown to be of the same order of magnitude as ordinary chemical compounds—such, for instance, as nitric oxide.

Strutt considers that active nitrogen is a monatomic variety of the element, produced by the action of the discharge employed, the yellow after-glow being a phenomenon attending the subsequent reversion of the active form to nitrogen possessing ordinary properties. In support of the monatomic nature of active nitrogen, no condensation is obtained on cooling the gas by means of liquid air, the pressure, measured by the "hardness" of the discharge, being unaltered by producing active nitrogen by means of an electrodeless discharge in a tube immersed in this cooling agent. It is highly improbable that a polyatomic body would be uncondensed under these conditions (*cf.* ozone). It may be noted, however, that Trautz* has recently put forward views on active nitrogen, according to which this body is regarded as possessing a molecular complexity corresponding to the formula N_3.

Strutt has measured the percentage of active nitrogen present in the gas leaving the discharge tube by two methods, involving absorption by phosphorus, and combination with nitric oxide respectively. In a determination carried out according to the first method, 2540 c.c. of nitrogen were passed through a weighed tube containing phosphorus, a portion of the tube being bent into the form of a U, and immersed in liquid air to prevent loss of phosphorus by volatilisation. An increase in weight of 15·5 mgrm. was obtained, corresponding to 12·2 c.c. of nitrogen, this being about 0·5 per cent. of the whole of the gas passed.

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* Z. f. Elektrochem., 1919, **25**, 299.

According to the second of the two methods employed, 540 c.c. of the nitrogen were allowed to react with excess of nitric oxide, the nitrogen trioxide, which is assumed to be formed according to the equations,

$$\begin{aligned} 2NO + N &= NO_2 + N_2 \\ NO_2 + NO &= N_2O_3 \end{aligned}$$

being condensed at − 180° C. In order to eliminate errors due to solution of excess of nitric oxide in the trioxide, this was allowed to warm up to − 50° C. before closing the apparatus for weighing. At this latter temperature dissolved nitric oxide boils off, the trioxide being, however, non-volatile under these conditions. From the experiment given 90 mgrm. of nitrogen trioxide were obtained, corresponding to a content of active nitrogen in the gas employed amounting to 2·46 per cent. This figure is higher than that for the determination made by means of phosphorus, but Strutt points out that it is extremely difficult to keep conditions constant from experiment to experiment.

Tiede and Domcke* have examined the behaviour of nitrogen of a very high degree of purity under the above conditions, and, as a result of their investigations, arrived at the important conclusion that nitrogen, which is free from every trace of oxygen, does not exhibit the phenomena which were obtained by Strutt.

In order to obtain nitrogen of this high degree of purity, Tiede and Domcke prepared the gas by the decomposition of barium or potassium azide. By taking special precautions, it was also found possible

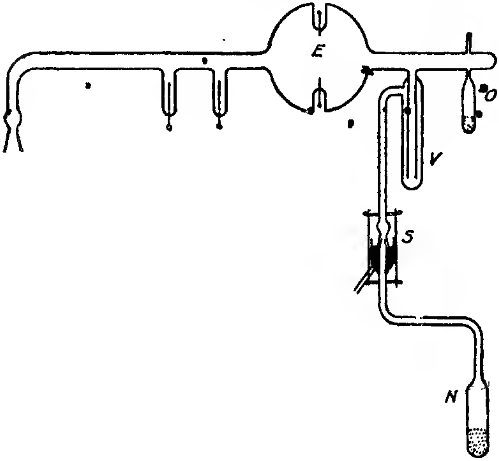
* Ber., 1913, 46, 340, 4095; 1914, 47, 420.

to purify nitrogen sufficiently by means of heated copper in order to obtain a suppression of the afterglow.

The apparatus employed by Tiede and Domcke is shown in Fig. 16.

It consists of a discharge tube E, which is connected, as shown, to a side tube N, containing dry

FIG. 16.



barium azide, which formed the source of nitrogen. O is a second side tube, in which was placed a small quantity of silver oxide, by means of which the nitrogen could be mixed with a trace of oxygen when desired. V is an absorption tube, containing gold leaf, in order to prevent the possibility of the penetration of potassium or barium vapour from N into the discharge tube. During the actual experiment V was cooled by immersion in liquid air, and in some instances the ground-in joint S was replaced by a fused joint. In any case no tap grease was used on S, this being rendered gas-tight by the mercury seal alone. The coil employed had a spark-length of 15 cm., and was operated with 8 ampères at a tension of 10 volts. A larger coil, of 30 cm. spark-length, provided with a Wehnelt interruptor, was also used.

Before beginning an experiment, the apparatus was evacuated by means of a Gaede pump. During this process the whole of the glass parts, with the exception of N and O, were heated to as high a temperature as possible by means of a bunsen flame, in order to free the surface of the glass from the difficultly removable water film and from adsorbed gases, the electrodes being also freed from occluded gas by heating these to redness by means of an intensified discharge. N was also heated for a short time to 120° by means of a paraffin bath, and the glass parts of the apparatus once more heated by a bunsen flame, in order to remove adsorbed traces of impurities which might have been given off by the azide.

After this process of preliminary purification the action of the pump was continued and the azide was raised to 170°, the induction discharge being put into operation. It was frequently noticed at the beginning of an experiment, even after the careful purification described, that the characteristic yellow after-glow was obtained, this being caused by small traces of impurities in the first portions of nitrogen given off by the azide, but on rinsing out the apparatus two or three times with nitrogen, for instance at a pressure of 40 mm., evacuating between each rinse, the after-glow became fainter and finally disappeared.

The pressure employed during the actual experiment was usually a few millimetres of mercury, corresponding to that used by Strutt, this pressure being regulated as required by the temperature to which the azide was heated.

In order to cause an intense reappearance of the yellow after-glow, the silver oxide, contained in o, was heated gently by means of a small flame, and on ceasing to heat this, the glow once more disappeared, this appearance and disappearance being reproducible as often as was desired.

In place of barium or potassium azide, it was found possible to purify commercial nitrogen by means of heated copper, provided that the temperature of this was maintained below that at which copper oxide undergoes appreciable dissociation this being, however, surprisingly low.

The following table illustrates the influence of the temperature of the copper purification tube on the glow obtained. It will be seen that at comparatively low temperatures the glow is either yellowish white or intensively yellow, due to the non-reactivity of the copper with oxygen. As the temperature of the copper is increased this begins to remove oxygen, and the glow in the discharge tube gradually disappears, but on heating the copper to a still higher temperature dissociation of copper oxide sets in, and the glow, owing to the presence of oxygen in the nitrogen, disappears.

TABLE XXVI.

Working pressure in mm.	Appearance of after-glow, with copper at temperature given.					
	Yellowish white.	Intense yellow.	After-glow disappearing.	After-glow absent.	After-glow reappearing.	Intense yellow.
2	—	20°	—	Above 325°	—	Above 575°
4	—	20°	325°	Above 370°	470°	Above 520°
6	20° (weak)	260°	360°	Above 430°	480°	Above 580°
12	20° (intense)	300°	420°	—	500°	Above 685°

The dependence of the after-glow on the presence of traces of oxygen was also noticed by Lewis* and by Comte.† Strutt‡ states that nitrogen may be obtained sufficiently free from foreign gases to resist activation by a condensed discharge, by allowing commercial nitrogen to stand for several hours in contact with molten sodium at 300° in the apparatus illustrated in Fig. 15. On allowing small quantities of oxygen, methane, ethylene, carbon dioxide or monoxide, hydrogen sulphide, mercury vapour, or indeed a trace of almost any admixture, to enter the system by means of a side tube, a gas was produced which could readily be activated. The activation of nitrogen is thus one of the many reactions which do not take place with pure substances only and these results are reminiscent of Baker's classical observations on the effect of the absence of water vapour on chemical reactions generally.

Indications of the existence of a modification of active nitrogen, which is apparently different from that formed by electric discharge at low pressures, have been obtained by Usher and Venkateswaran§ during the electrolysis of solutions of sodium azide. A somewhat similar preparation of what from its mode of formation may possibly be the complex N_3 was obtained also by Brown and Lundell,‖ who state that the nitrogen evolved at the anode during the electrolysis of potassium azide in anhydrous azoimide at −78° attacks mercury.

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* *Loc. cit.*

† Phys. Z., 1913, **14**, 74.

‡ J. Chem. Soc., 1918, **113**, 200.

§ J. Chem. Soc., 1919, **115**, 613.

‖ J. Am. Chem. Soc., 1909, **31**, 435.

SUBJECT INDEX

Active nitrogen, 102
— — effect of temperature on, 104
— — formation of nitrides from, 104, *et seq.*
— — preparation of, by electrolysis, 112
Aluminium nitride, 74
Amalgams, use of, for nitride formation, 5[illegible], 66
Amides, decomposition of, 58
Ammonia, apparatus for the synthesis of, 11, 15, 18, 22, 23, 24, 40, 44
— equilibrium constant, variation with temperature of, 5, 12, 14, 19
— — determination of, 9
— heat of formation of, 2, 8
— molecular heat of, 6
— presence of, in the sun, 37
— synthesis of, at high temperatures, 37
— — by silent discharge, 46
— — in water-cooled flames, 43
— variation with temperature of equilibrium percentage of, 14, 20
Antimony nitride, 87
Arsenic nitride, 86

Barium nitride, 65
Beryllium nitride, 67
Bismuth nitride, 87
Boron nitride, 72

Cadmium nitride, 70
Calcium nitride, 65
Carbon subnitride, 78
Catalysts, destruction of activity of nitrogen by, 106
Cerium, catalytic activity of, 35
— nitride, 81
Circulating system for synthesis of ammonia, 24
Chromium nitride, 88
Cobalt nitride, 101
Copper nitride, 62
— oxide, dissociation of, 101
Cyanogen, 77
— employment of, for nitride formation, 57, 67

Gold nitride, 65

Halogen nitrides, 94
Hydrogen, specific heat of, 6

Iron, catalytic activity of, 26, 28, 32, 34
— nitride, 96

Lanthanum nitride, 76
Lead nitride, 83
Lithium nitride, 61

Magnesium nitride, 67
— — interaction of, with oxides of carbon, 68
Magnetic properties of iron containing nitrogen, 99
Manganese, catalytic activity of, 36
— nitride, 93
Mercury nitride, 70
Molybdenum nitride, 86

Nickel nitride, 100
Niobium nitride, 85
Nitrides, direct synthesis of, 49
— general methods for preparation of, 49

Nitrides, general properties of, 58
— normal formulæ of, 59
— thermal formation of, 52
Nitrogen, influence of percentage of, on velocity of formation of ammonia, 30
— bromide, 95
— chloride, 94
— iodide, 95
— selenide, 91
— specific heat of, 6
— sulphides, 91, 105
— telluride, 91

Osmium, catalytic activity of, 25, 33
Oxygen, effect of, on activation of nitrogen, 106, 108, *et seq.*

Paracyanogen, 77
Phosphorus nitride, 86
Potassium nitride, 62
Pressure, influence of, on velocity formation of ammonia, 31

Rare earths, nitrides of, 75
Rubidium nitride, 62

Silver nitride, 64
Sodium nitride, 62
Strontium nitride, 65

Tantalum nitrides, 85
Temperature, influence of, on velocity of formation of ammonia, 28, 29
Thorium nitride, 82
Tin nitride, 83
Titanium nitride, 79
Tungsten, catalytic activity of, 36
— nitride, 89

Uranium, catalytic activity of, 34
— carbide, catalytic activity of, 26, 27, 29, 30, 31
— nitride, 89

Vanadium nitrides, 84
Variation of equilibrium ammonia percentage with pressure and temperature, 20
— of ammonia equilibrium constant with temperature, 5

Zinc nitride, 69
Zirconium nitride, 89

NAME INDEX

Arons, 70
Austin, 6

Baerfuss, 45
Baker, 112
Bassett, 63
Beilby, 63, 97, 100, 101
Berthelot, 2, 46
Berthollet, 64
Berzelius, 79
Blix, 73
Bougrand, 77
Brieglieb, 67, 74, 88, 98
Briner, 38, 45, 46
Brown, 112
Buff, 96
Bort, 105

Caron, 67
Chattaway, 95
Clever, 91
Comte, 112

Davies, 46
Deslandres, 49
Despretz, 96
Deville, 37, 67, 72, 78, 79
Dixon, 37
Domcke, 108 *et seq.*
Donkin, 46

Eidmann, 72
Engelhardt, 79

Ferée, 50, 88
Fichter, 68
Fischer, 52, 62, 70, 72, 83, 87
Fowler, 37, 97, 98, 100
Frankland, 69
Franklin, 58, 71, 87
Frémy, 98
Fresenius, 95

Gattermann, 94
Gautier, 66
Gay Lussac, 58, 62
Geuther, 67, 74, 78, 88, 98
Goldstein, 102
Greenwood, 26, 29, 30, 31

Haber, 2, 4, 6, 8, 10, 11, 13, 14, 15, 18, 19, 21, 23, 26, 29, 30, 31, 32, 34, 35, 44
Hartog, 100
Henderson, 63, 97, 100, 101
Henning, 6
Hentschel, 94
Hirzel, 71
Hoff, van't, 1, 8
Hoffmann, 71, 86
Holborn, 6
Hugot, 86, 95

Iliovici, 52, 83, 87

Jacquemin, 77

Kahn, 38
Kirschbraun, 69, 74, 97
Kirchhoff, 1, 6
Koenig, 44, 46
Kohlschütter, 83, 89
Kraft, 76, 81

Le Blanc, 46
Le Rossignol, 10, 11, 13, 14, 16, 18, 19, 21, 23, 32, 34, 35
Lewis, 102, 112
Limb, 66
Lundel, 112
Lyon, 94

Maquenne, 65, 66
Marburg, 71
Maschke, 11, 13, 14
Matignon, 2, 75, 76, 81, 83
Matthews, 80
Maxted, 26, 28, 31, 38, 39, 43, 45, 46, 97, 98
Merz, 68
Mettler, 38
Metzner, 91
Moeser, 72
Moissan, 80, 83, 85, 89
Morell, 77
Morren, 102
Muthmann, 76, 81, 84, 85, 91

Noyes, 94

Oeholm, 2
Oordt, van, 10
Orton, 95

Perman, 45
Plantamour, 70
Ponnaz, 16, 19
Prelinger, 50, 93

Raschig, 64, 65
Regnault, 6
Riedelbauch, 84, 85
Rodet, 105
Rogstadius, 96
Roscoe, 84, 85

Sarasin, 102
Schenk, 91
Schoelly, 68
Schonbein, 95
Schröter, 52, 62, 70, 72, 83, 87
Schrotter, 62, 88
Schutzenherger, 79
Serpek, 74
Smits, 57, 63
Stahlschmidt, 98
Stock, 73, 86
Strutt, 102 *et seq.*, 106, 110, 112

Tamaru, 2, 6, 16, 19
Thénard, 58, 62
Thomsen, 2
Tiede, 108 *et seq.*
Titherley, 62
Trautz, 107

Uhrlaub, 84, 89
Usher, 112

Venkateswaran, 112
Verneuil, 91
Vournasos, 67, 101

Warburg, 102
Wedekind, 81
Weiss, 79
White, 67, 74, 97
Wiedemann, 6
Wöhler, 72, 78, 79, 80, 89, 91
Wolk, 98

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